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FURTHER STUDIES ON THERMAL REPULSION

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(Communicated by Dr. L. A. Ramdas, F.A.SC.)

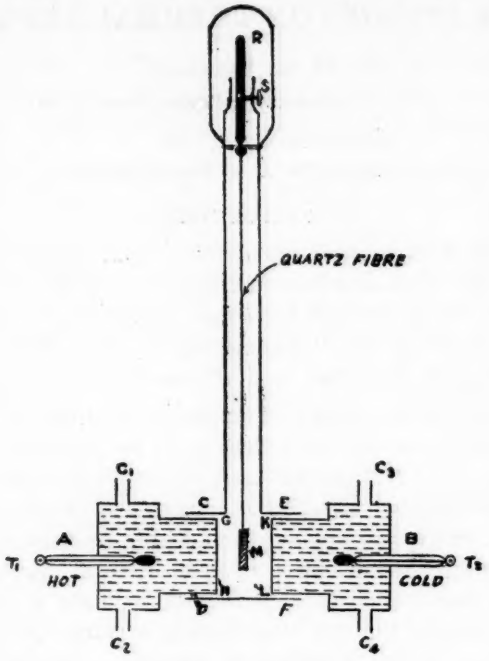
1. Introduction

Ramdas and co-workers pointed out early in 1931 that both above and below a heated plate there is a dust-free layer of very hot air. Above the plate this layer shoots up through the colder air above in a regular pattern forming what is known as the "shimmering layer". This aspect of the subject has been further developed and discussed in a series of papers.[1,2,3]

Below the heated plate, owing to the stable arrangement of the air layers, the convective phenomena are not violent as in the previous case but very much simpler. In fact, when matters are so arranged that an air cell (filled with smoke and illuminated suitably) is formed with a hot surface above and a cold surface below and the sides are suitably enclosed, the dark layer is found to be restricted in its scope by a pair of vortices. As the cold lower surface is brought nearer and nearer to the hot surface it is found that the vortices separate towards the two sides leaving a calm layer at the centre where the dark layer attains a maximum thickness; ultimately, when the cold surface approaches the hot one within 2 mm. or less the vortices die away completely, all convective phenomena cease, and thermal repulsion has full play. When this "convection-free" state is reached, dust particles are repelled with a uniform velocity as defined by Stokes' Law and are deposited on the cold plate. The velocity is found to be proportional to the thermal gradient. These results have been discussed fully in a paper[4] by the present writer. Later, Ramdas and Joglekar[5] studied the movements of oil droplets in a vertical convection-free air cell (between a vertical hot surface and a vertical cold surface) and found that the falling particles being acted upon by gravity vertically and by the thermal repulsive force horizontally, move in straight lines inclined to the vertical from the hot to the cold surface.

In the same paper they have described experiments on the steady deflection of a mica vane suspended parallel to the two surfaces by means of quartz fibre. The mica vane is repelled from the hot towards the cold

surface, the deflections being proportional to the temperature gradient. The apparatus used in the above experiment is shown in Fig. 1.



THERMAL REPULSION APPARATUS.

FIG. 1

A temperature gradient is maintained between the faces GH and KL of the vessels A and B which are kept at the desired temperatures by circulating hot and cold water respectively through the pipes C_1, C_2, C_3 and C_4; T_1 and T_2 are thermometers. The vessels A and B slide in the outer piece CEFD so that the distance between GH and KL may be adjusted as desired. The joints at C, D, E and F are made air-tight by means of a mixture of bees-wax and rosin. The mica piece M is suspended by means of a fine quartz fibre as shown in the figure. As soon as the face GH becomes warmer than KL, M is deflected to the right, the deflection being proportional to the temperature difference when the air cell is thin enough to be convection-free, as it is always arranged to be in all the experiments to be described hereafter. The deflections are measured by means of a microscope focussed on the lower end of the quartz fibre and having a suitable scale in the eye-piece.

The experiments of Ramdas and Joglekar were made at atmospheric pressure. At the suggestion of Dr. Ramdas the present writer undertook the detailed investigation of thermal repulsion at different pressures ranging from atmospheric pressure to 10^{-4} cm. of Hg. The influence of the size of the gap between the hot and cold surfaces, effect of different gases, etc., have also been investigated over the entire range of pressure referred to above. The results so far obtained are discussed in the present paper.

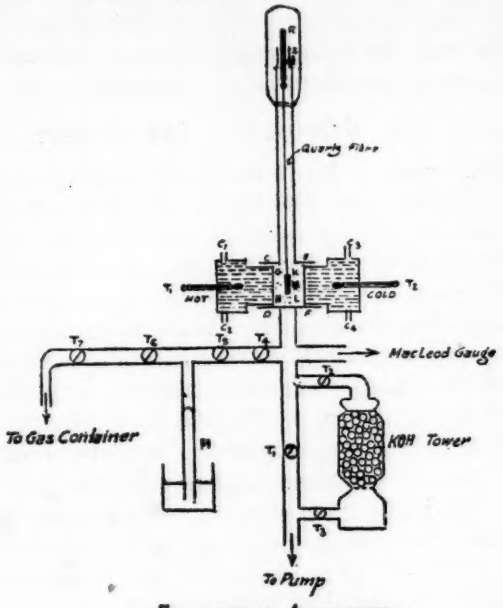
2. Experimental Arrangements

The apparatus shown in Fig. 1 was found to be very convenient for the present work. The inter-space GH KL was provided with two diametrically opposite glass windows through which a beam of light coming nearly perpendicular to the plane of the diagram from below illuminated the junction of the quartz fibre and the mica piece. The gap was also provided at the top with an inlet tube for evacuation and introducing other gases. For reducing gas pressure a Gaede High-Vacuum Pump was used. A specially constructed MacLeod gauge designed to measure pressures in the range 8×10^{-2} cm. of Hg to 10^{-4} cm. of Hg was used. Pressures higher than 8×10^{-2} cm. were measured directly with a vertically travelling microscope focussed on the top of the mercury column in the MacLeod gauge when its Hg reservoir is kept in the lower position. Gas pressures were controlled during experiments by running the pump until the desired pressure was reached and by closing the stopcock between the apparatus and the pump. Gases were dried by allowing them to stand in tubes containing phosphorous pentoxide before being drawn into the experimental chamber. The temperatures of the hot and cold surfaces could be maintained constant to within 0·1° C., but actual temperature readings were always taken.

The general experimental arrangement is shown in Fig. 2.

The procedure followed in introducing a given non-corrosive gas was as follows:—T_2 and T_3 were kept closed. T_1, T_4, T_5, T_6 were opened and the air was pumped out until the pressure fell to about 10^{-4} cm. as indicated by the gauge. Then T_1, T_4, T_5 and T_6 were closed. T_7 was opened and gas was admitted into the P_2O_5 tube between T_6 and T_7. T_7 was closed and the gas allowed to stand in the tube for 15 minutes. Then T_6 was slightly opened and a small quantity (as indicated roughly by the fall of Hg in the manometer M) of gas let into the space between T_6 and T_5. Then T_6 was closed and T_5 opened so that gas filled the space between T_5 and T_4. Then T_5 was closed and T_4 opened so as to admit the gas into the experimental chamber. This precaution in introducing the gas was necessary in order to avoid the

mica vane being thrown into violent oscillations. After introducing the gas, it was pumped out. In this way, the apparatus was washed with the gas under experiment several times before the final filling was done. The thermal repulsion at different pressures was then observed. In the case of



EXPERIMENTAL ARRANGEMENT.

FIG. 2

corrosive gases the KOH tower was used for protecting the pump. To pump out the gases, T_1 was closed and T_2 and T_3 were opened. This was continued till the pressure fell to about 1 mm. of Hg. The tower packed as it was with small KOH tablets offered a large resistance to pumping. So to obtain lower pressures T_2 T_3 were closed and T_1 opened, the small residual gas not being expected to cause appreciable damage to the pump.

To enable sufficiently low pressures to be attained wide-bored glass-tubing was used for connecting the different parts of the apparatus and rubber-tubing avoided as far as possible.

3. VARIATION OF THERMAL REPULSION WITH PRESSURE IN AIR

Fig. 3 represents a typical curve showing the dependence of thermal pressure on the gas pressure. The distance between the hot and cold surface was 5 mm. The mica vane was in the middle of the gap. δ is the deflection

in divisions of the microscope eye-piece scale. ΔT is the difference of temperature between the surfaces. The length of the quartz fibre was 20·65 cm. and the mass of mica 5·8 mgm. The dimensions of the vane were 0·742 cm.

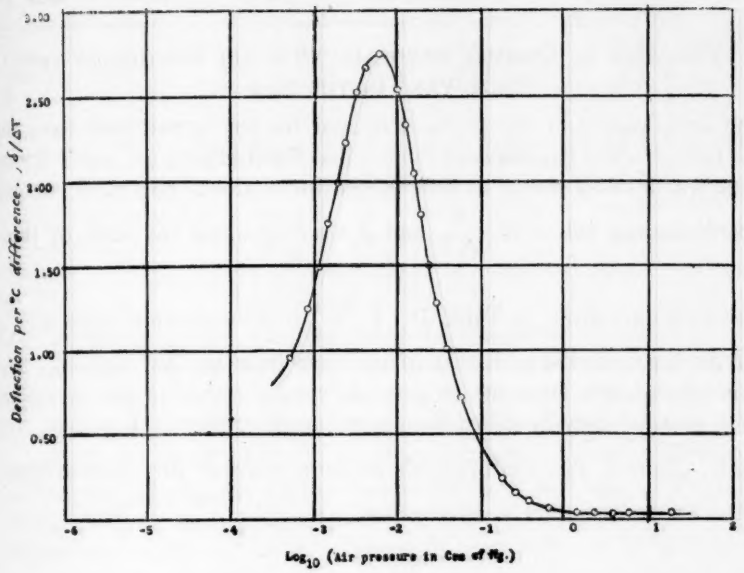


FIG. 3

(length) and 0·328 cm. (breadth). One division in the microscope scale equals 1/20 mm. Unit value of $\delta/\Delta T$ therefore corresponds to a thermal pressure of $5{\cdot}659 \times 10^{-3}$ dynes per cm.[2]

It will be seen that the deflection is very small at high pressures, but increases to a maximum as the air pressure is reduced to $6{\cdot}3 \times 10^{-3}$ cm. of Hg. The deflection decreases thereafter with further decrease of air pressure.

4. Variation of Thermal Repulsion with Temperature Difference

To study the dependence of thermal repulsion on ΔT a gap of 2·5 mm. was used. The mica vane was placed in the middle of the gap. The dimensions and mass of the mica vane as also the length of the suspension were the same as before. The air pressure was maintained at $6{\cdot}5 \times 10^{-2}$ cm. of Hg. The results are given in Table I. δ is the deflection of the vane, δ when plotted against ΔT will be seen to be proportional to the temperature difference. This proportionality is used in the succeeding sections to reduce the deflections for $\Delta T = 1°$ C.

TABLE I

ΔT in °C. ..	0·0	3·3	3·5	4·2	5·3	7·65
Deflection δ ..	0·0	9·0	7·8	10·5	11·6	18·5

5. Variation of Thermal Repulsion with the Position of the Mica Vane in the Gap

The mica vane and the suspension used for this experiment were the same as before. The gap between the hot and the cold surfaces was 7·5 mm. The vane was initially placed at different positions along the axis of the gap and corresponding values of $\frac{\delta}{\Delta T}$ and p were obtained for each of these positions.

The results are given in Table II. $\left(\frac{\delta_m}{\Delta T}\right)$ is the maximum value of $\frac{\delta}{\Delta T}$ and the distance referred to is that of the vane from the hot surface. The third row of the table gives the air pressure corresponding to the maximum deflection or what may be called the optimum air pressure. It will be seen that both $\frac{\delta_m}{\Delta T}$ and the optimum air pressure increase in value as either the hot or the cold surface is approached.

TABLE II

Distance from hot surface in mm.	1·30	2·5	4·25	5·5	6·9
$\delta_m/\Delta T$ ..	2·25	2·15	2·10	2·23	2·65
$p \times 10^3$ cm. of Hg ..	5·62	4·17	4·27	4·79	7·59

6. Effects of Varying the Width of the Gap

The experiment described in Section 5 was repeated with a number of gaps using the same vane and suspension as before. The whole of the data cannot be given here for considerations of space. It was however observed that if we restrict our attention to the same value of $\frac{Z}{g}$ (where Z is the distance of the vane from the hot surface and g the width of the gap) then the maximum deflections and the corresponding optimum pressures showed some interesting features. These are given in Table III for the case $\frac{Z}{g}$ nearly equal to 0·5. g is the gap in mm. It will be seen that $g \times \frac{\delta_m}{\Delta T}$ (where δ_m is the maximum deflection) has a mean value of 15·53. It increases from 12·9

for a small gap of 1·25 mm. to 17·0 for a gap of 10 mm. but remains constant for bigger gaps.

Again one notices a gradual but slight increase in the value of $g \times p_m$.

TABLE III

Gap in mm. ..	1·25	2·5	5	7·5	10·0	11·25	15·0	20·0
Gap × $p_m \times 10^2$ ..	3·13	3·46	3·15	3·20	3·54	3·56	3·77	3·55
Gap × $\delta_m/\Delta T$ ..	12·9	13·1	14·5	15·8	17·0	17·5	16·5	17·0

7. VARIATION WITH THE AREA AND PERIMETER OF THE VANE

TABLE IV

$-\text{Log}_{10} p$ ..	1	1·4	1·6	1·8	2·0	2·2	2·4	2·6	2·8	3·0	3·2	3·4
$(\delta/\Delta T)_1$ / $(\delta/\Delta T)_2$	1·33	1·18	1·18	1·20	1·24	1·24	1·22	1·28	1·4	1·37	1·4	1·55

Rectangular mica vanes were used for this purpose. Table IV refers to a comparison of results with two mica vanes over a wide range of air pressures. The first had an area of 100 mm.^{2} Its dimensions were 1 cm. × 1 cm. and mass 18·4 mgm. The length of the suspension was 25·2 cm. The other vane had an area of 45 mm.^{2} Its dimensions were 1·5 cm. × ·3 cm. and mass 9·9 mgm. The length of the suspension was 25·5 cm. The first row in Table IV gives the air pressure and the second row gives the ratio of the deflections in the two cases. This ratio is seen to be fairly constant over the wide range of pressures experimented with. This indicates that thermal forces bear a sensibly constant ratio at all pressures.

Table V gives the values of $\frac{m}{l} \times \frac{\delta_m}{\Delta T}$ for a number of mica vanes, m, l being respectively the mass and the length of the suspension. $\frac{m}{l} \times \frac{\delta_m}{\Delta T}$

TABLE V

Perimeter mm. ..	14·0	21·2	33·4	36·0	40·0
Area in mm.^{2} ..	12·0	23·7	27·0	45·0	100·0
$\frac{m}{l} \times \frac{\delta_m}{\Delta T}$ ..	0·45	0·79	0·91	1·34	2·86

is proportional to the maximum thermal force. The table also gives the perimeter and the area of the vanes. The thermal force seems to be proportional to the area. There is no simple relation between the thermal force and the perimeter. Thermal force does not, therefore, appear to be an edge effect. It is area effect, under the "convection-free" conditions of our experiments.

8. Experiments with Mica and Aluminium Vanes

To study the effect of the conductivity of the material of the vane, the experiment was done with a mica vane and later with an aluminium vane. Both had nearly the same area. The dimensions of the Al vane were $1{\cdot}05 \times 0{\cdot}95$ cm. Its mass was 48 mgm. and suspension length $22{\cdot}0$ cm. The mica vane had dimensions 1 cm. $\times$ 1 cm. Its mass was $18{\cdot}4$ mgm. and the suspension length $25{\cdot}2$ cm. Fig. 4 represents the results obtained.

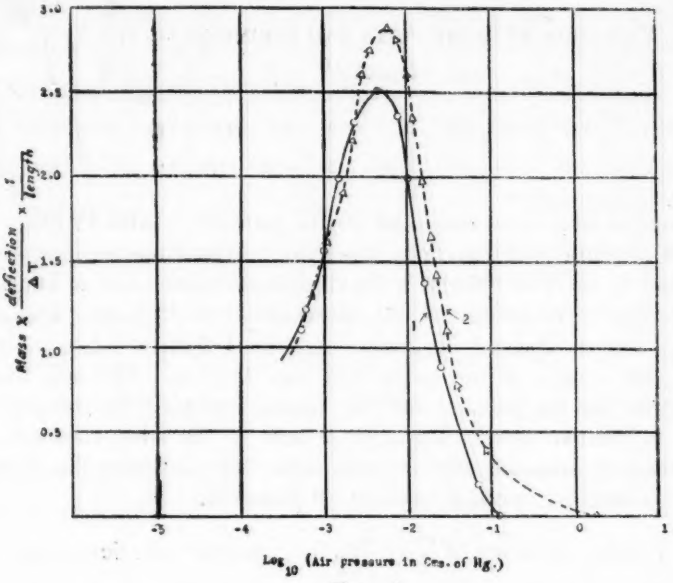


Fig. 4

Curve 1 refers to aluminium and curve 2 refers to mica. The force on aluminium is slightly less than on mica. In comparison with the ratio of thermal conductivities of the two materials $\left(\frac{\text{conductivity of aluminium}}{\text{conductivity of mica}}\right.$ $= \frac{\cdot 514}{\cdot 0018} = 285{\cdot}6$), the change in thermal repulsion seems to be slight.

9. Variation with Different Positions of the Vane along a Diameter of the Cylindrical Chamber

A series of measurements were made with the mica vane at different positions along a vertical diameter of the chamber, but equidistant from the two surfaces. The results obtained showed that there is no appreciable variation with the position of the vane along this direction.

10. Vane Placed with its Plane Perpendicular to the Plane of the Hot or Cold Surface

In Fig. 5, Curve 1 shows the results when the vane is parallel to the hot surface and Curve 2 shows the results when the vane is perpendicular to the

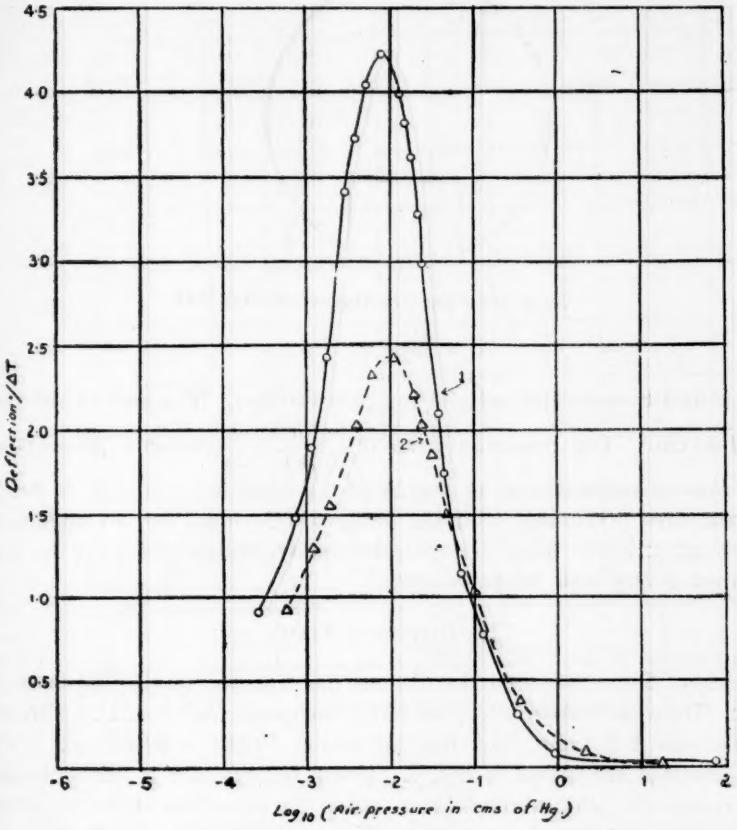


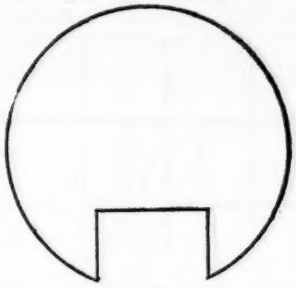
Fig. 5.

hot surface. The maximum thermal repulsion in the latter case is roughly half of that when the vane is parallel to the surface.

11. Large Aluminium Vane

The diameter of the circular chamber is 7·25 cm. In all the previous experiments the area of the vane was very small as compared to the area of the hot or cold surface. To study what happens when the area of the vane

approaches that of the hot surface, an aluminium blade of the shape given in Fig. 6 was used. It is a thin circular disc of radius 3·25 cm. with a rectangular cut 2·5 cm. × 1·5 cm. to allow free space for the glass separating



Shape of the Largest Alluminium Vane Used.

Fig. 6

pieces placed between the hot and the cold surfaces. The area of the vane was 29·44 cm.^{2} The maximum value of $\frac{m}{l}\cdot\frac{\delta}{\Delta T}\times\frac{1}{A}$ (which is proportional to the ratio of thermal force to area A of the vane) was found to be 0·024. This compares favourably with the value 0·025 found for an aluminium blade 1 cm. × 1 cm. Thus the proportionality of thermal force to area holds over a very wide range of areas.

12. Different Gases

A gap of 5 mm. was used. In all cases the vane was kept in the centre of the gap. The vane was of mica and had dimensions ·742 × ·32 × ·016 cm. Its mass was 5·8 mgm. and the suspension length = 20·65 cm. The results obtained are shown in Fig. 7. It will be seen that as the molecular size increases, the peak becomes lower and at the same time shifts to the low pressure side. In Fig. 8, the values of $\delta_m/\Delta T$ (maximum deflection per degree difference of temperature) are plotted against the mean free path at N.T.P. which is inversely proportional to the area of molecular cross-section. The values are the means of two sets of observations. The curve is a straight line passing close to the origin. In Fig. 9, the abscissæ are $\log_{10}$ of the optimum gas pressures. From the graph it can be deduced that

$$\frac{\delta_m}{\Delta T}=56\cdot23\times p_m^{0\cdot89}=56\cdot23\times p_m^{0\cdot6}\text{ nearly.}$$

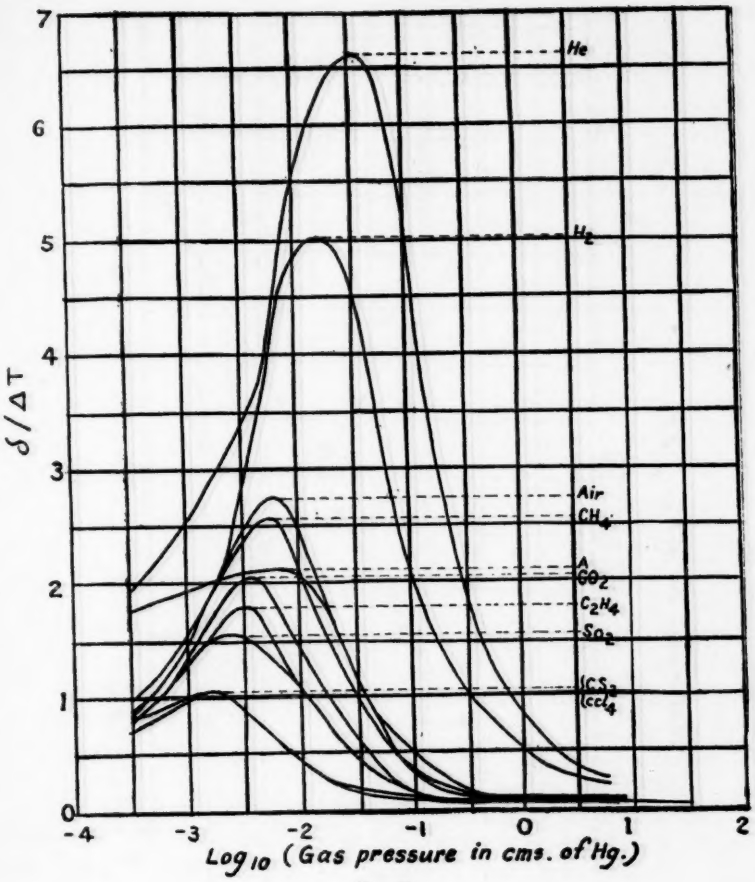


FIG. 7

13. GENERAL DISCUSSION OF RESULTS

(*a*) In the experiments described above, a vertical gas cell is used. As shown in a previous paper by the present author, a vortex motion is present at atmospheric pressure if the gap is not small enough. If the gas pressure is reduced sufficiently, a stage is reached when the vortex motion will cease whatever be the width of the gap. The wider the gap the lower the pressure will have to be reduced to for attaining the "convection-free" state. For the purpose of the present paper, it is quite safe to assume that at pressures below 1 mm. of Hg convectional movements are entirely absent. In an air cell without convective movements the air is stratified into vertical strata

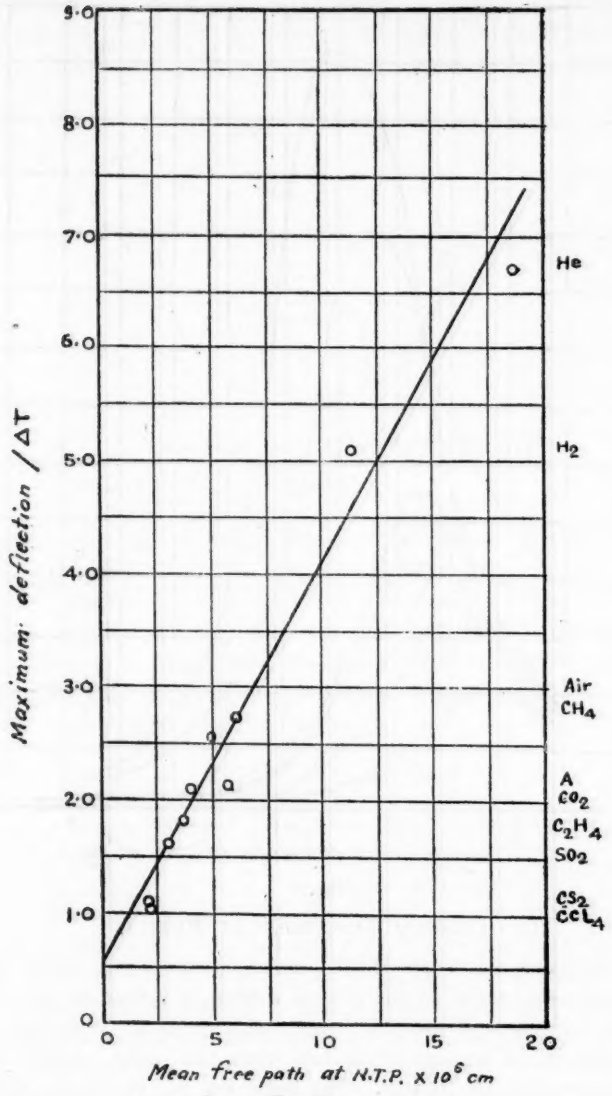


FIG. 8

at different temperatures and the heat conduction proceeds under the ideal conditions imagined in deducing the conductivity formula in the kinetic theory of gases.

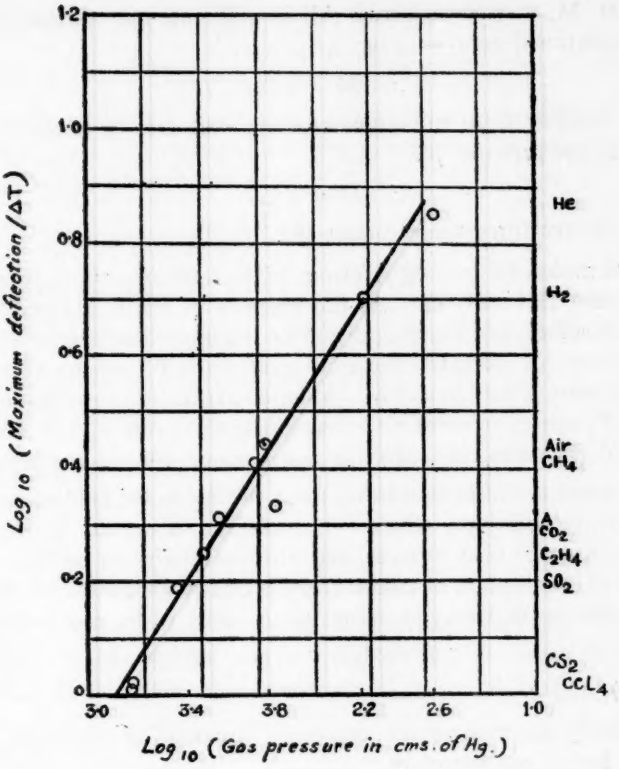


FIG. 9

An attempt will now be made to derive an expression for the thermal pressure starting from some elementary considerations and to use it to explain the important features of the phenomenon described in the foregoing sections.

In Fig. 10 let HH be the hot surface and CC the cold surface. Imagine unit area AB parallel to HH. This area is crossed by the same number of molecules per second in either direction. Denote this number by 'n'. The molecules crossing AB from left to right are more energetic than those crossing AB from right to left. Naturally there will be a net transfer of momentum from left to right across AB. This momentum will clearly be proportional to 'n'. Again the molecules crossing AB from left to right may be supposed to have, on an average, a temperature t_1 appropriate to some such plane as P_1. Similarly we may suppose P_2 to be the equivalent plane on the right-hand side and let the temperature there be t_2. Then the

momentum 'M' transferred across AB in unit time may further be assumed to be proportional to $t_1 - t_2$ or Δt

$$\therefore \quad M \propto n \, \Delta t$$

Now the number 'n' of molecules crossing unit area is known to be proportional to gas pressure 'p'.

$$\therefore \quad M \propto p \, \Delta t$$

We now observe three things about Δt.

(i) The molecules crossing AB from left to right are coming from different strata between HH and AB. As the pressure of gas is reduced, the mean free path increases, and the proportion of the molecules coming from larger distances from AB increases, the equivalent plane P_1 moving nearer to HH and thus increasing the value of t_1. A similar argument shows that as pressure decreases, P_2 moves towards CC, decreasing the value of t_2. Thus as gas pressure 'p' decreases, the effective temperature difference increases.

(ii) Imagine a molecule to travel from the hot to the cold surface. Then it suffers $\pi\sigma^2 g\nu$ collisions, where σ is molecular diameter, 'g' the distance between the hot and cold surfaces, and ν is the number of molecules per c.c. The degree of equalisation of kinetic energies clearly increases with the number of these collisions and may therefore be assumed to be proportional to

$$a_1 + b_1 (\pi\sigma^2 g\nu) + c_1 (\pi\sigma^2 g\nu)^2,$$

where a_1, b_1 and c_1 are constants.

Δt will clearly decrease as the degree of equalisation of kinetic energies increases. Let us put therefore

$$\Delta t \propto \frac{1}{\text{degree of equalisation of kinetic energies}}$$

$$\text{or} \quad \Delta t \propto \frac{1}{a_1 + b_1 (\pi\sigma^2 g\nu) + c_1 (\pi\sigma^2 g\nu)^2}.$$

But $\nu \propto p$ and therefore we may write

$$\Delta t \propto \frac{1}{a_1' + b_1' (\pi\sigma^2 gp) + c_1' (\pi\sigma^2 gp)^2},$$

where a_1', b_1' and c_1' are constants.

This is obviously consistent with the idea in (i).

(iii) Again Δt may be assumed to be proportional to ΔT, the temperature difference between the hot and the cold surfaces.

$$\therefore \quad \text{We put} \quad \Delta t \propto \frac{\Delta T}{a_1' + b_1' (\pi\sigma^2 gp) + c_1' (\pi\sigma^2 gp)^2}.$$

But we have seen that $M \propto p \Delta t$.

Therefore $$M \propto \frac{p\Delta T}{a_1' + b_1'(\pi\sigma^2 gp) + + c_1'(\pi\sigma^2 gp)^2}.$$

If we now suppose that a vane of some material is suspended in the position AB, then this vane will experience a thermal pressure proportional to M. We therefore have thermal pressure

$$P = \frac{ap\ \Delta T}{1 + b(\sigma^2 gp) + c(\sigma^2 gp)^2} \tag{1}$$

a, b and c being constants.

We will now examine how far (1) explains "the observed results".

It can be shown by differentiating the above with respect to p, that 'P', regarded as a function of 'p', has a maximum at $p = \frac{1}{\sqrt{c}\, g\sigma^2}$. This explains the hump observed in Section 3. The proportionality of 'P' to ΔT (when 'p' is kept constant) described in Section 4 also follows from (1). The optimum pressure

$$p_m = \frac{1}{\sqrt{c}\, g\sigma^2} \tag{2}$$

so that $p_m \times g$ = a constant for a given σ, *i.e.*, for a given gas. This was the result found in Section 6. If now we substitute this optimum value of 'p' in (1) then the maximum thermal pressure

$$P_m = \frac{(a\ \Delta\ T)/\ (\sqrt{c}g\sigma^2)}{2 + \frac{b}{\sqrt{c}}}. \tag{3}$$

If the gap is varied, then $P_m \times g$ is a constant. This is another result found in Section 6.

In Sections 7 and 11 we have seen that the thermal force is proportional to area. This hardly needs any explanation after reading through our derivation of equation (1).

If the vane is thin enough to enable us to suppose that its two sides do not differ very much in temperature, then it is immaterial as to what the material is. This is roughly what we find in Section 8.

From equation (1) it will be seen that as the gas pressure p tends to zero the thermal pressure P tends to be equal to $ap\ \Delta T$. This expression is independent of σ and therefore independent of the gas used. Here reference may be made to the work of Lockenvitz.[6] He shows that the thermal pressure

at very low gas pressure is given by

$$P = \frac{p \Delta T}{4T}.$$

This is independent of the particular gas used. We thus see that equation (1) gives as a limit the formula of Lockenvitz.

Let us now consider results for different gases described in Section 12. The maximum deflection $\delta_m/\Delta T$ (which is proportional to the maximum thermal pressure) was there seen to be proportional to the mean free path at N.T.P., *i.e.*, $\lambda \propto \frac{1}{\sigma^2}$.

$$\text{Therefore } \frac{\delta_m}{\Delta T} \propto \frac{1}{\sigma^2}. \tag{4}$$

This result follows from (3) above.

Thus formula (1) represents most of the experimental results.

Consider now the optimum gas pressure p_m as given by (2).

$$p_m = \frac{1}{\sqrt{c\, g \sigma^2}}.$$

$$\text{But } P_m \propto \frac{1}{\sigma^2}.$$

Therefore on our theory we expect $P_m \propto p_m$. On reference to Section 12 it will be seen however that the verdict of the experiment is

$$P_m \propto p_m^{0.6} \quad \text{approximately.}$$

Thus in this respect, although the theory given above does predict correctly that p_m increases with P_m, the fit is not quantitative.

(*b*) We shall now consider the experimental results described in Section 5. Mandell and West[7] have shown that the fall of temperature from the hot to the cold surface is not exactly linear. They have shown that the temperature falls more rapidly near the hot and cold surfaces than in the middle. It is natural to expect that the thermal force on the suspended vane will be varying similarly to the temperature gradient in its neighbourhood. This explains the larger deflections obtained when the vane approaches either surface.

(*c*) *Explanation of the results in Section* 10.—We have seen that even when the vane is placed perpendicular to the hot surface, there is quite a large thermal repulsion, the maximum value being about one half of what we get when the vane is parallel to the surface. This result may appear

to be rather puzzling at a first glance. One is apt to think that the thermal force when the vane is perpendicular to the hot surface should be vanishingly small. The following considerations, however, show that the deflection

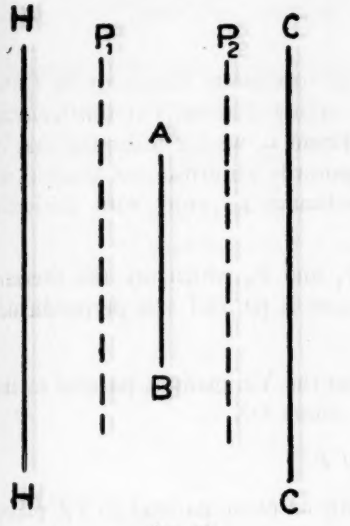


FIG. 10

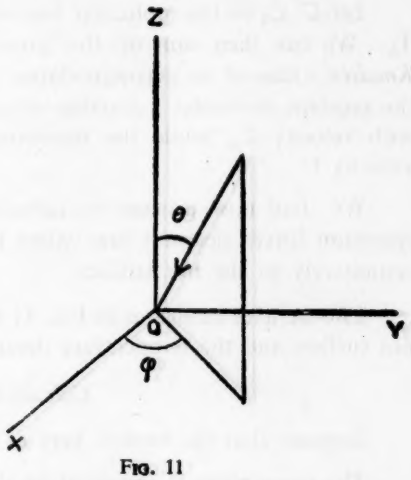


FIG. 11

actually observed in the perpendicular position is to be expected. We make the following assumptions:—

(1) Let n be the number of molecules striking or leaving unit area of a solid surface in unit time. Then we suppose with Knudsen[8] that the number whose velocity directions lie in a narrow cone of solid angle $d\omega$ whose axis makes an angle ψ with the normal to the surface is given by $\frac{n}{\pi}\cos\psi\, d\omega$.

(2) The molecules coming from the hot surface side and the cold surface side have mean velocities C and C_1 respectively, C being $> C_1$; C_0 is the velocity of a molecule corresponding to the temperature T_0 of the vane.

(3) Consider a solid surface at temperature T_0 in contact with a gas. Let the mean temperatures of the incident and reflected molecules be T and T′ respectively. Then if α is Knudsen's accommodation coefficient,

$$\alpha = \frac{T' - T}{T_0 - T}.$$

Let us now suppose that a fraction x of the incident molecules is absorbed and then re-emitted with the temperature T_0 and that the others

are re-emitted without any alteration of temperature. Then the mean temperature of the outgoing molecules $= x\,T_0 + (1-x)\,T$ and this must equal T′. Substituting this value of T′ in the equation for α we get,

$$\alpha = \frac{x\,T_0 + (1-x)\,T - T}{T_0 - T} = x.$$

Let C, C_0 be the molecular velocities appropriate to temperatures T and T_0. We can then sum up this point by saying that *without contradicting Knudsen's* idea of an accommodation coefficient α, we are assuming that of the incident molecules a fraction α is temporarily absorbed and then leaves with velocity C_0, while the remaining molecules go away with unaltered velocity C.

We shall now proceed to calculate P_1 and P_2 which are the thermal repulsion forces per unit area when the vane is parallel and perpendicular respectively to the hot surface.

Choose axes as shown in Fig. 11 so that the YZ plane is parallel to the hot surface and the temperature decreases along OX.

Calculation of P_1

Suppose that the vane is kept at O with its plane parallel to YZ plane.

The momentum P_1 imparted by the molecules in unit time per unit area of the vane is made up of the following parts on the X side of the YZ plane.

(i) Momentum due to n molecules incident.

(ii) Momentum due to $(1-\alpha)\,n$ molecules leaving with unaltered velocity.

(iii) Momentum due to αn molecules leaving with velocity C_0. There will be three similar contributions say—(i)′, (ii)′ and (iii)′ due to X′ side of the YZ plane. Since (iii) and (iii)′ are equal and opposite their joint result $= 0$.

Consider (i) and (ii). The result is clearly the same as that of $n + (1-\alpha)\,n$ molecules or $n(2-\alpha)$ molecules being incident. Same is true of (i)′ and (ii)′.

Thus P_1 = Momentum due to $n(2-\alpha)$ molecules of velocity C_1 incident on X side of YZ plane and

Momentum due to $n(2-\alpha)$ molecules of velocity C incident on X′ side of YZ.

Write $n' = n(2-\alpha)$.

Now the number of molecules incident along $(\theta, \phi, d\omega)$ in the octant **XYZ**

$$= \frac{n'}{\pi} \sin\theta \cos\phi \, d\omega$$

$$= \frac{n'}{\pi} \sin^2\theta \cos\phi \, d\theta \, d\phi.$$

The momentum due to each molecule of this group parallel to **OX**

$$= -m c_1 \sin\theta \cos\phi$$

$$\therefore P_1 = -4 \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{\pi/2} \left(\frac{n'}{\pi} \sin^2\theta \cos\phi \, d\theta \, d\phi\right) mc_1 \sin\theta \cos\phi$$ due to 4 octants on the **X** side of **YZ** plane

$$+ 4 \int_{\theta=0}^{\pi/2} \int_{\phi=\pi/2}^{\pi/2} \left(-\frac{n'}{\pi} \sin^2\theta \cos\phi \, d\theta \, d\phi\right) (-mc \sin\theta \cos\phi)$$ due to the 4 octants on the **X′** side of **YZ** plane.

$$= \frac{4n'm}{\pi} \int_0^{\pi/2} \sin^3\theta \, d\theta \left[c \int_{\pi/2}^{\pi} \cos^2\phi \, d\phi - c_1 \int_0^{\pi/2} \cos^2\phi \, d\phi\right]$$

$$= \frac{4n'm}{\pi} \times \frac{2}{3}\left(c\frac{\pi}{4} - c_1\frac{\pi}{4}\right)$$

$$= \tfrac{2}{3} n'm(c - c_1)$$

$$= \tfrac{2}{3} n(2 - \alpha) m(c - c_1) \text{ since } n' = n(2 - \alpha).$$

Calculation of P_2

Suppose the vane to be placed at **O** with its plane parallel to **ZX** plane.

P_2 is made up of the following parts:—

(i) Momentum due to n molecules incident on both sides of the vane.

(ii) Momentum due to $n(1 - \alpha)$ molecules diffusely leaving the vane without any alteration of the incident velocity on both sides of the vane.

(iii) Momentum due to αn molecules diffusely leaving either side with velocity C_0.

The effect of (iii) is clearly zero. Regarding (ii) it can be shown by considering any single group of incident molecules that on leaving diffusely they impart a momentum perpendicular to the vane. Further there is symmetry about the **ZX** plane and therefore the net result is zero.

$\therefore$ P_2 is due to (i) only.

$$\therefore \quad P_2 = -4\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{\pi/2}\left(\frac{n}{\pi}\sin^2\theta\sin\phi\,d\theta\,d\phi\right) mc_1 \sin\theta\cos\phi$$ due to the 4 octants on the X side of YZ plane

$$+4\int_{\theta=0}^{\pi/2}\int_{\phi=\pi/2}^{\pi}\left(\frac{n}{\pi}\sin^2\theta\sin\phi\,d\theta\,d\phi\right)(-mc\sin\theta\cos\phi)$$ due to the 4 octants on the X′ side of the YZ plane

$$= -\frac{4nm}{\pi}\int_0^{\pi/2}\sin^3\theta\,d\theta\left[c_1\int_0^{\pi/2}\sin\phi\cos\phi\,d\phi + c\int_{\pi/2}^{\pi}\sin\phi\cos\phi\,d\phi\right]$$

$$= -\frac{4nm}{\pi}\times\tfrac{2}{3}\times\left[\frac{c_1}{2}-\frac{c}{2}\right]$$

$$= \tfrac{4}{3}\frac{nm}{\pi}(c-c_1).$$

$\therefore$ We have $\dfrac{P_1}{P_2} = (2-\alpha)\dfrac{\pi}{2}$

If we suppose that $\alpha = 1$, then $\dfrac{P_1}{P_2} = \dfrac{\pi}{2}$.

If $\alpha = 0$, $\dfrac{P_1}{P_2} = \pi$.

The experimental values obtained so far for α range from 1 to about 2·4.

The above results suggest that we have here a new experimental method of investigating the accommodation coefficient.

Summary and Conclusion

Using a suspended vane between a hot and a cold surface, a study has been made of thermal repulsion under ideal 'convection-free' conditions. The dependance of the force on area, orientation and material of the vane, size of the gap, the position of the vane relative to the gap as also the nature of the gas has been studied. An explanation of the observed effects has been offered. It has also been shown that the variation of thermal repulsion when the vane is parallel and perpendicular respectively offers a new experimental method of investigating the accommodation coefficient.

In conclusion, the author desires to express his indebtedness to Dr. L. A. Ramdas for suggesting the problem and for his interest in the work. The

author also wishes to thank the Director-General of Observatories for permission to work in the Laboratory of the Meteorological Office at Poona. The author also wishes to place on record his thanks to Prof. M. G. Mahajan of the Nowroji Wadia College, Poona, for the loan of a megavac pump and to Prof. B. V. Bhide of Sir Parashurambhau College, Poona, for facilities given in the preparation of gases.

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DETERMINATION OF THE ELASTIC CONSTANTS OF ISOTROPIC MEDIA: A NEW METHOD

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1. Introduction

The determination of the elastic constants of isotropic substances by dynamical methods has been the subject of investigation by several workers. In most of such methods, the material was used in the form of a rod and ultrasonic waves were transmitted through it by attaching a piezoelectric quartz to one of the ends. Rohrich[1] made a complete determination of the velocity of ultrasonic waves in steel, brass, copper, aluminium and glass. His experiments were continued by Schoeneck[2] who investigated the elastic longitudinal vibrations in single crystals.

More exact determinations of the elastic constants of transparent bodies were carried out by Schæfer and Bergmann.[3] In this method, both longitudinal and shear waves are excited and the corresponding diffraction patterns observed. The method has been extended also to opaque substances.

It was recently observed[4] in this laboratory that characteristic thickness shear modes could also be transmitted through the crystal plates and communicated to liquids in the form of consequential longitudinal strains. This has suggested the possibility of exciting shear modes in thin plates of isotropic substances as well and detecting them by optical methods if they could similarly be communicated to a liquid.

2. Experimental Method and Observations

Using a tourmaline wedge with a frequency range of 3 to 16 megacycles per second, the characteristic transmission frequencies of several plates of glass, steel, brass and platinum have been studied by the method of ultrasonic diffraction, the details of which have been described in earlier papers.[5] Plates of different sizes and of the same thickness have been examined in each case with a view to see if the size has any effect on the intensity of the shear modes. In order to avoid errors due to the mounting, the wedge is chosen to be a size smaller than the smallest of the specimens used. Both the longitudinal and shear fundamental frequencies could easily be detected and

measured in transmission if the plates chosen are sufficiently thin and small. The elastic constants C_{11} and C_{44} are then evaluated. Using the well-known relations of transformation, the Young's modulus y and the rigidity modulus n may be obtained for each material. In the case of glass the values thus obtained are compared with the values obtained by separate static experiments on the same specimen in this laboratory. Comparison for the rest is effected by taking the values from standard tables. It may be noted here that practically all the substances showed an increase in intensity of shear modes with smaller areas of the specimen plates. This supports our view that shear modes are communicated as corresponding longitudinal strains to the adjoining liquid due to a coupling effect arising in these cases from the finite size of the plates. The shear modes are comparatively weak in soft metals like brass whereas they are very bright in glass and steel, sometimes being equal in intensity to the longitudinal ones. The fundamental frequencies of the longitudinal and shear modes and the calculated values of C_{11} and C_{44} are given in Table I for different materials.

TABLE I

Material	Thickness in mm.	Fundamental frequency of longitudinal mode. Megacycles per second	Fundamental frequency of torsion mode. Megacycles per second	Density	$C_{11} \times 10^{-10}$ dynes/cm.^{2}	$C_{44} \times 10^{-10}$ dynes/cm.^{2}
Glass ..	0·93	3·22	1·40	26·02	93·2	17·6
Steel ..	0·64	4·80	2·60	7·502	287·0	84·0
Brass ..	0·58	4·20	1·745	8·56	203·0	35·0
Platinum ..	0·16	13·30	5·335	20·99	380·2	61·1

The values of y and n deduced from the above data along with the experimental static values of glass and the standard values taken from tables in the other cases are given in Table II.

TABLE II

Material	Authors' results		Static values	
	y	n	y	n
Glass ..	4·80	1·76	4·60	1·80
Steel ..	21·71	8·40	19 to 21	7·7 to 8·3
Brass ..	9·77	3·50	9·7 to 10·2	3·5
Platinum ..	17·16	6·11	16·80	6·10

The unit is 10^{11} dynes per cm.^{2}

3. Discussion

The smallest size of the plate used in the above investigation is 6 mm. square. The method is simple and sufficiently accurate, being particularly suitable for substances available only as small bits. The possibility of investigating the elastic properties of precious metals, alloys and other such materials under varying physical conditions is obvious. The exact mechanism by which the shear mode in the plate is communicated as a longitudinal wave to the liquid medium is of theoretical interest and requires to be further investigated. Examination of plates of different sizes has shown that edge coupling of the plates is probably the cause.

4. Summary

A new method of determining the Young's modulus and the rigidity modulus of isotropic materials using ultrasonic frequencies has been deseribed. Results obtained with glass, steel, brass and platinum by such a method compare well with the standard values. Only a small plate of about 6 mm. square of the material is all that is required and hence the method is capable of being utilized under varying physical conditions in respect of rare and precious specimens.

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OPTICAL ACTIVITY IN CRYSTALS: APPLICATION OF GROUP THEORY

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(Communicated by Prof.S. Bhagavantam, F.A.SC.)

1. Introduction

A phenomenological description of all physical properties of crystals which can be represented by a tensor can be given by simple group theoretical methods. The number of independent constants needed to describe the photo-elastic, elastic and optical properties of each of the 32 crystal classes was thus derived by Bhagavantam (1942). Piezo-electricity was similarly dealt with by Bishambhar Dayal Saksena (1944). The author (1945) has independently extended the method to the cases of piezo-electricity and electro-optical Kerr effect. In this note, the case of optical activity is dealt with.

2. Optical Activity

The scalar parameter g which represents the optical activity or rotation per unit thickness of the crystal in the direction l, m, n, is given by

$$g = g_{11} l^2 + g_{22} m^2 + g_{33} n^2 + 2 g_{23} mn + 2 g_{31} nl + 2 g_{12} lm,$$

where g_{ik} $(i, k = 1, 2, 3)$ are the components of the gyration tensor which is known to be symmetric. These six components which describe the optical activity in the most general case of a triclinic crystal, reduce to a smaller number as other symmetry elements are introduced. It is an experimental fact that the rotation of plane of polarization is independent of the sense of travel, but the rotation of plane of polarization changes sign by the application of a symmetry operation involving a reflection and remains unchanged by a mere rotation about any axis. In order, therefore, to find the number of independent constants required to specify the gyration tensor, we should find the number of independent and orthogonal linear combinations of g_{ik}'s which will transform under each symmetry operation characteristic of the crystal class so as to remain invariant if the symmetry operation is a pure rotation and change sign if the symmetry operation is a rotation-reflection. The character appropriate to the gyration tensor is the same as that used in

earlier references in respect of symmetric tensors of second order and is $4\cos^2\phi \pm 2\cos\phi$. By applying the well-known theorem for finding the number of combinations that will occur under the appropriate irreducible representation, we obtain

$$n_i = \frac{1}{N} \sum_j h_j \chi_j'(R)\, \chi_i(R)$$

where $\chi_j'(R) = 4\cos^2\phi \pm 2\cos\phi$ and $\chi_i(R) = \pm 1$,

according as R is a pure rotation or a rotation-reflection. The summation extends over all the symmetry elements characteristic of the crystal class under investigation.

3. Results and Discussion

Applying the above formula, it can immediately be seen that the 11 classes with a centre of symmetry (C_i, C_{2h}, D_{2h}, C_{4h}, D_{4h}, S_6, D_{3d}, C_{6h}, D_{6h}, T_h, O_h) exhibit no optical activity. Of the remaining 21 classes, six more (C_{4v}, C_{2v}, C_{3h}, D_{3h}, C_{6v}, T_d) do not show optical activity and the others have constants ranging from six to one. The actual numbers are given below and in all cases, they agree with the numbers derived directly (Szivessy, 1928; Wooster, 1938).

C_1	6
C_2	4
D_2	3
C_s, C_4, S_4, D_4, C_3, D_3, C_6, D_6	2
C_{2v}, D_{2d}, T, O	1

It is with great pleasure that the author offers his grateful thanks to Prof. S. Bhagavantam for his kind encouragement.

4. Summary

The group theoretical method given by Bhagavantam has been extended to derive the number of independent constants needed to describe optical activity in the 32 crystal classes.

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PREPARATION OF PENTAMMINO CUPRIC SULPHATE FROM AMMONIACAL SOLUTIONS OF COPPER SULPHATE

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(Communicated by Dr. Satya Prakash, D.Sc., F.A.Sc.)

The study of the cupric-ammines has attracted the attention of a large number of workers, who have prepared and studied these compounds by various means. The existence of di-, tetra-, and penta-ammino compounds are well established. In a recent communication Bhattacharya and Dey[1] have reported the existence of cupric hexammino-sulphate as well in ammoniacal solutions of copper sulphate and attempts for its isolation are being made.

When an aqueous solution of ammonium hydroxide is added to a solution of cupric sulphate, cupric hydroxide precipitates first, which dissolves in excess of ammonia giving a deep blue liquid called eau celeste. Numerous studies have been made on this liquid. Immerwahr[2] has suggested that in solution the $Cu^{\cdot\cdot}$ ions get replaced by more complex cupric-ammino $Cu(NH_3)_n^{\cdot\cdot}$ ions. Reychler[3] from freezing point measurements found that the complex ions behave more or less in the same way as the $Cu^{\cdot\cdot}$ ions. Konowaloff,[4] Gaus,[5] and Locke and Forssall[6] by absorption and vapour pressure experiments found the compound to be $Cu(NH_3)_4SO_4$. Dawson and McCrae[7] determined the distribution ratio between water and chloroform and found the $Cu : NH_3$ ratio to be 1 : 4. Horn[8] supported the existence of the tetra-ammino compound and said that the $Cu : NH_3$ ratio could never be greater than 1 : 4. This result is, however, definitely contradicted by the existence of the now well-known pentammino compound and of the hexammino compound as found by Dey and Bhattacharya. In addition to the aforesaid workers, Blanchard[9] studied the blue liquid from viscosity data and Bouzat[10] from thermal data and obtained the evidence of the existence of cupric tetrammino sulphate in the solution. More recently Job[11] by absorption spectra studies determined the composition and found that it corresponded to that of the tetrammino compound. Glasstone[12] by electrometric titration of copper sulphate with aqueous ammonia obtained evidence of the presence of $Cu(NH_3)_4^{\cdot\cdot}$ ions. Bhatnagar, Goyle and Prasad[13] however say that the blue colour of the cuprammino complex is due to copper-hydroxide in colloidal form.

Quite a number of methods are known for the isolation of the ammino-complexes from aqueous solution. Berzelius[14] recommended the addition of alcohol to an ammoniacal solution of copper sulphate when the compound separates out in pulverulent crystals. Bouzat[15] cooled a hot concentrated solution of the salt and quickly dried the crystals between filter-papers. Andre[16] prepared the salt by passing ammonia gas into a solution of copper sulphate. Horn and Taylor[17] and Dawson (*loc. cit.*) recommended this process. Pickering[18] obtained the compound by adding aqueous ammonia to an almost saturated solution of cupric sulphate until the precipitate of cupric hydroxide just redissolved and allowing the solution to stand for some time.

The process of preparation in this study was that described by King.[19] The compound precipitated by alcohol was decomposed by caustic soda solution and the precipitated copper oxide filtered and estimated. The expelled ammonia was passed into a standard acid solution and ammonia thus estimated. The Cu : NH_3 ratio was found to be 1 : 5 thus suggesting the formula of the compound to be $Cu(NH_3)_5SO_4$, and not $Cu(NH_3)_4SO_4$ as reported by previous workers.

Experimental

10 Grams of finely powdered pentahydrated cupric sulphate (A.R. quality) was dissolved in a mixture of 10 c.c. water and 15 c.c. Merck's ammonia solution (sp. gr. 0·888). To this well stirred blue solution were added 15 c.c. of alcohol from a dropping funnel. The ammino compound separated out as a dark blue crystalline meal. This was filtered in a Buchner's funnel, washed thoroughly with alcohol and kept in a desiccator over lime.

The ammonia present in the solid was determined by the Kjeldahl's distillation method and the copper was determined gravimetrically as copper oxide. The following analytical values for the ratio of copper to ammonia were obtained:

Ratio		Total Analysis	
Cu : NH_3		Found	Calculated
1 : 5·057	Copper ..	26·04%	25·98%
1 : 4·993	Ammonia ..	34·64	34·76
1 : 4·986	Sulphate ..	39·01	39·36
1 : 5·053			
1 : 5·048		99·69	100·00

On estimation of sulphate, the ratio $Cu : SO_4$ was found to be 1 : 1; water of crystallisation was found to be absent. It is evident that the compound obtained by us has the formula $Cu(NH_3)_5SO_4$.

The pentammino compound as prepared by us smells of ammonia even at ordinary temperatures and it is evident that it slowly decomposes. The surface layer of the salt gradually changes to bluish white even when the salt is preserved in a desiccator over lime. The salt dissolves in water giving a deep blue solution, but hydrolyses on further addition of water and gives a precipitate of hydroxide. When the deep blue solution is heated there is a brisk evolution of ammonia and a black deposit of cupric oxide is formed.

Summary and Conclusion

The compound precipitated by the addition of alcohol to an ammoniacal solution of cupric sulphate was known to be cupric tetrammino sulphate. In this study this compound has been analysed and has been shown to be $Cu(NH_3)_5SO_4$.

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SYNTHESIS OF 5:6:7-HYDROXYFLAVONES AND THEIR DERIVATIVES—PART I

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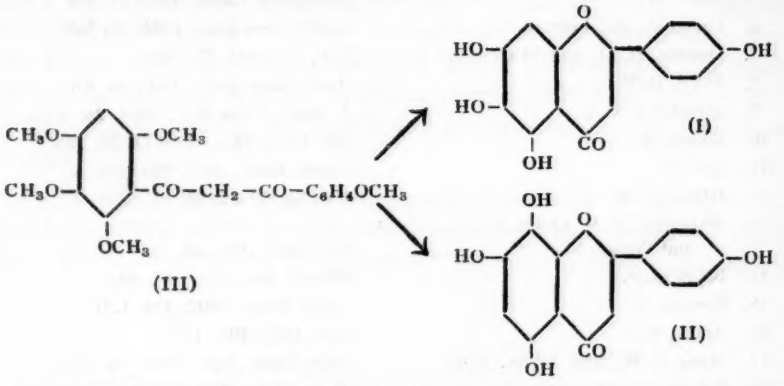
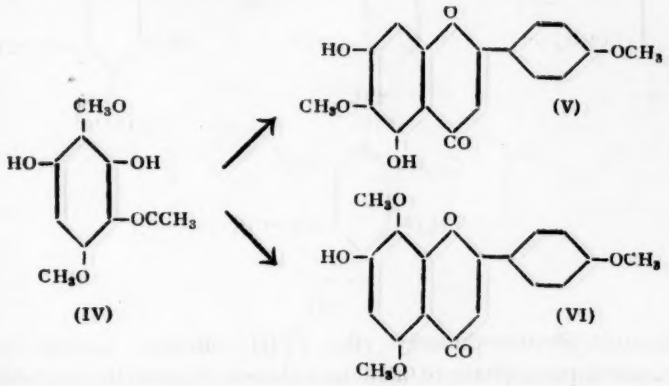
Of the possible flavones with the 5:6:7-arrangement of hydroxyls in the benzopyrone part only two are so far known to occur in nature either free or combined. They are baicalein and scutellarein. The latter was the first to be discovered and studied. It was isolated by Molisch and Goldschmiedt[1] from the leaves and flowers of *Scutellaria altissima*; it has also been found in the leaves and flowers of *S. baicalensis*. Its constitution was investigated by Goldschmiedt and Zerner[2] who concluded that it should be either 5:6:7:4′-(I) or 5:7:8:4′-tetrahydroxy flavone (II). This was confirmed by the synthesis of Bargellini[3] who submitted pentamethoxy-dibenzoylmethane (III) to the action of hydriodic acid. The reaction could proceed in two ways, but actually scutellarein alone was obtained. This synthesis, however, did not enable the choice to be made between the two alternatives.



The trihydroxy flavone, baicalein was obtained from the roots of *S. baicalensis* by Shibata, Iwata and Nakamura[4] and it has also been found to be present in the root and stem barks of *Oroxylum indicum*.[4] It resembles scutellarein closely in its properties. The substance had already been synthesised by Bargellini[5] following the method adopted by him for scutellarein. Of the two possible isomers only one was again obtained

and that was given the 5 : 6 : 7-constitution. The main point mentioned in favour of this was that the product was not identical with hydroxy-chrysin obtained by Nierenstein[6] by the oxidation of chrysin and considered by him to be 5 : 7 : 8-trihydroxy flavone. Since Nierenstein's claim was later shown to be wrong, this support lost its significance. Hattori[7] who later repeated the above synthesis of Bargellini was not able to confirm the older observations regarding the exclusive formation of scutellarein from the diketone (III). Similar results were obtained by him even with regard to the baicalein synthesis. Consequently the previous synthetic support for the constitution of these compounds could not be considered definite.

Wessely and Moser[8] attempted to supply more definite evidence for the constitution of scutellarein by the synthesis of 5 : 7 : 8 : 4′-tetrahydroxy flavone in an unambiguous manner. For this purpose 2 : 4-dihydroxy-3 : 6-dimethoxy acetophenone (IV) was heated with the anhydride and sodium salt of anisic acid according to the method of Allan and Robinson. The product was, however, found to be a dimethyl ether of scutellarein (V) and this extraordinary result was attributed to initial demethylation in the ortho-position of the ketonic group and subsequent ring closure favouring the 5 : 6 : 7-arrangement. Thus even in this method complications were found to exist. In one of the large number of experiments, however, such demethylation did not occur and the normal condensation product, 7-hydroxy-5 : 8 : 4′-trimethoxy flavone (VI) was produced.

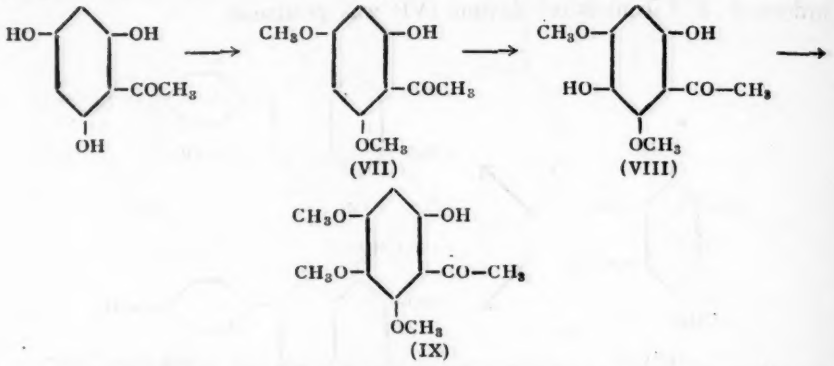


An unequivocal proof for the constitution of scutellarein was provided by Robinson and Schwarzenbach[9] who synthesised its tetramethyl ether by a novel method in which the 4-aminoderivative of the corresponding flavylium salt was an intermediate. This method, however, involves the preparation of

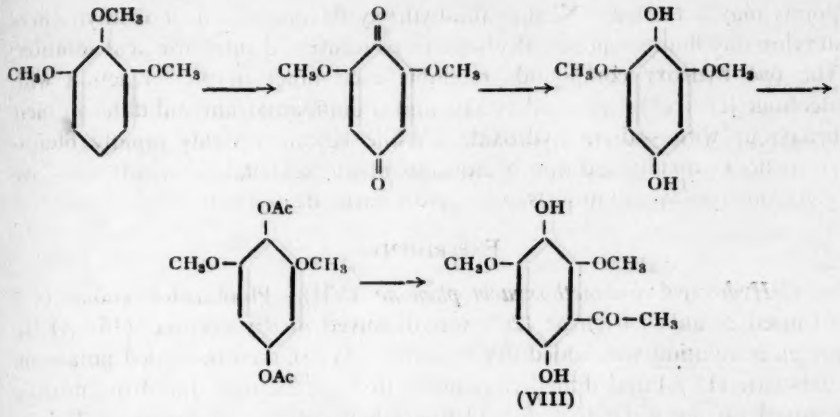
aroyl-pyruvamides which are not easily accessible and hence has not been generally employed for the synthesis of flavones.

In view of the position reviewed above, a simple and at the same time unambiguous method of synthesis of the 5:6:7-hydroxyflavones seemed to be needed. One such method which will also be useful for the study of the partial methyl ethers of baicalein and scutellarein has now been worked out. The required ortho-hydroxy ketone has been prepared by an unambiguous method and converted into the flavones by adopting the Baker-Venkataraman[10] procedure which is free from complications. The constitution of the products are therefore free from doubt and the work reported in this paper therefore provides unequivocal confirmation of the constitutions of baicalein and scutellarein.

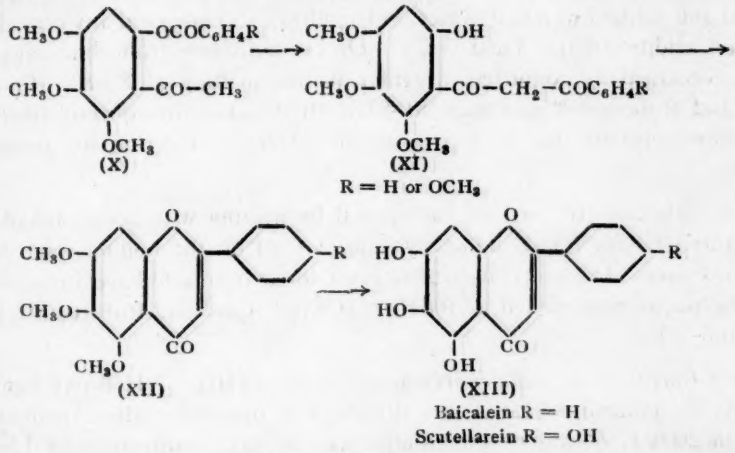
2-Hydroxy-4:5:6-trimethoxyacetophenone (IX) has now been prepared starting from phloroacetophenone and passing through the stages indicated below. Phloroacetophenone is subjected to partial methylation using the requisite amounts of dimethyl sulphate and potassium carbonate. The 4:6-dimethyl ether (VII) is obtained in good yield. This compound was originally made by Kostanecki and Tambor[11] by the partial demethylation of phloroacetophenone trimethyl ether and was subsequently obtained by Canter, Curd and Robertson[12] along with the *p*-hydroxy isomer by the Hoesch condensation of phloroglucinol dimethyl ether with acetonitrile.



Phloroacetophenone-dimethyl ether (VII) undergoes smooth oxidation with potassium persulphate in alkaline solution to give the 2:5-dihydroxy compound (VIII) in good yield. The constitution of this ketone is arrived at not only from analogy with a large number of similar cases[13], but is supported by its reactions. This compound was obtained earlier by Mauthner[14] starting from pyrogallol trimethyl ether and proceeding as indicated below:



The new method of preparation seems to be definitely better. The final stage is partial methylation converting the dihydroxy ketone (VIII) into (IX).[13] Its benzoyl and anisoyl derivatives (X) undergo rearrangement into the ortho-hydroxy diketones (XI) in the presence of sodamide in toluene solution and ring closure to the flavones (XII) is effected by heating with glacial acetic acid and sodium acetate. Demethylation with boiling hydriodic acid yields baicalein and scutellarein (XIII).



The hydroxy compounds and the methyl ethers have all the properties recorded for baicalein, scutellarein and their derivatives. The synthetic baicalein and its derivatives have been compared with samples obtained from *Oroxylum indicum* and found to be identical.. The following important

points may be noted. Neither the hydroxy flavone nor their methyl ethers develop any fluorescence in alcoholic or concentrated sulphuric acid solution. The two hydroxy compounds resemble each other in their reaction with alcoholic ferric chloride, lead acetate and sodium amalgam and differ in their behaviour with sodium hydroxide. While baicalein yields rapidly bluish-green flocks on the addition of aqueous alkali, scutellarein dissolves to give a greenish yellow solution which rapidly turns deep green.

Experimental

2-Hydroxy-4: 6-dimethoxyacetophenone (VII).—Phloracetophenone (4·2 g.) dried in an air-oven at 120°, was dissolved in dry acetone (15 c.c.); to the clear solution was added dry benzene (75 c.c.), freshly ignited potassium carbonate (15 g.) and dimethyl sulphate (6·5 g.; 2·2 mols.) and the mixture refluxed on the water-bath for 12 hours with occasional shaking. The inorganic salts were then filtered and washed with hot benzene. The filtrate was washed twice with water, (20 c.c.) each time, and then extracted with 5% aqueous sodium hydroxide four times. The united alkaline extract was poured into ice-cold dilute hydrochloric acid when 2-hydroxy-4: 6-dimethoxy acetophenone was precipitated as a practically colourless crystalline mass. It was filtered and thoroughly macerated with 5% aqueous sodium carbonate to remove any monomethyl ether that might have been formed, and again filtered and washed well with water. (The filtrate did not yield any crystalline solid on acidification). Yield, 3·2 g. On crystallisation from dilute alcohol it was obtained as colourless irregular prisms melting at 82–83° (Canter, Curd and Robertson[10] give m.p. 81–82°). It dissolved in aqueous alkali to an yellow solution and gave a brownish-red ferric reaction in alcoholic solution.

The substance (0·5 g.) was acetylated by heating with acetic anhydride (5 c.c.) and freshly fused sodium acetate (1·0 g.) on the boiling water-bath for two hours. The acetyl derivative crystallised from ethyl acetate as stout rhombic prisms and melted at 106–107° (Canter, Curd and Robertson[12] give m.p. 106–7°).

2: 5-Dihydroxy-4: 6-dimethoxy-acetophenone (VIII).—2-Hydroxy-4: 6-dimethoxy-acetophenone (15 g.) was dissolved in aqueous sodium hydroxide (20 g. in 200 c.c. of water), the solution cooled to a temperature of 15–20° and kept continuously stirred. A solution of potassium persulphate (22 g.; 1·1 mol.) in water (300 c.c.) was then introduced dropwise during the course of 4 hours, the temperature being maintained at 15–20° throughout the reaction. After allowing to stand for 24 hours, the dark reddish-brown

reaction mixture was rendered distinctly acid to litmus by the addition of concentrated hydrochloric acid. The unreacted original ketone which was precipitated as a dark brown crystalline solid, was filtered and washed with a small quantity of water. The clear aqueous filtrate was treated with sodium sulphite (5 g.) and animal charcoal (3 g.) and again filtered after stirring well for about 5–10 minutes. Concentrated hydrochloric acid (150 c.c.) was then added and the solution heated on the boiling water-bath for ½ hour. On cooling it rapidly deposited a brownish yellow crystalline mass which was collected, and washed with water. Yield, 5 g. The filtrate was twice extracted with ether and the solvent distilled when a further quantity (1 g.) of the dihydroxy-compound was obtained. If the solution should be heated on the water-bath for a longer duration (1 hour) for the hydrolysis, the product obtained was very deep brown in colour and was difficult to purify. When twice crystallised from aqueous alcohol using animal charcoal the substance was obtained as stout yellow rhombic prisms melting at 164–65° (Mauthner[14] gives m.p. 162–63°). It was moderately soluble in hot water, more so in alcohol and acetone, but sparingly soluble in light petroleum. Its solution in aqueous sodium hydroxide was bright yellow and turned deep reddish-brown on keeping. In alcoholic solution the substance gave a transient green colouration with ferric chloride which rapidly became reddish-brown either on keeping or on the addition of a slight excess of the reagent. No precipitate was obtained with lead acetate in alcoholic solution. (Found: C, 56·8; H, 5·4; $C_{10}H_{12}O_5$ requires C, 56·6; H, 5·7%.)

2 : 5-*Dibenzoyloxy*-4 : 6-*dimethoxy acetophenone*.—Dry pyridine (8 c.c.) and benzoyl chloride (1·5 g.) were added to the above *p*-dihydroxy acetophenone (1·0 g.) and the mixture heated on the boiling water-bath for 20 minutes. It was added to ice-cold water containing a few c.c. of hydrochloric acid and the precipitated brown solid collected, washed with water and crystallised twice from alcohol in which it was moderately soluble. The dibenzoate was thus obtained as colourless thick aggregates of micaceous plates and it melted at 153–54°. The substance did not dissolve in cold aqueous alkali and gave no colour with ferric chloride in alcoholic solution. (Found: C, 68·4; H, 5·1; $C_{24}H_{20}O_7$ requires C, 68·6; H, 4·8%.)

2-*Hydroxy*-4 : 5 : 6-*trimethoxy acetophenone* (IX).—The 2 : 5-dihydroxy-compound (2 g.) was dissolved in a mixture of dry acetone (10 c.c.) and dry benzene (75 c.c.) and to this solution were added acid-free dimethyl sulphate (1 c.c.; 1·1 mol.) and freshly ignited potassium carbonate (6 g.). The mixture was heated under reflux for 12 hours, the inorganic salts filtered and washed with a small quantity of hot benzene. The benzene filtrate was

washed with 5% aqueous sodium carbonate in order to remove any unmethylated dihydroxy-compound and then extracted with 10% aqueous sodium hydroxide. The united alkaline extracts were acidified with ice-cold (1 : 1) hydrochloric acid when the partially methylated ether was obtained as a reddish-brown oil. It was taken in ether, the ether solution dried over sodium sulphate and the solvent distilled. The residue was then treated with light petroleum (b.p. 40–60°) when the last traces of unchanged dihydroxy compound were precipitated. After allowing to stand for an hour, the petroleum ether solution was carefully decanted and the solvent was distilled off; 2-hydroxy-4 : 5 : 6-trimethoxy acetophenone was left behind as an yellow oil. Yield, 1·5 g. It dissolved in aqueous sodium hydroxide to an yellow solution and gave a deep violet brown colour with ferric chloride in alcoholic solution (*cf.* Baker[13]).

2-*Benzoyloxy*-4 : 5 : 6-*trimethoxy acetophenone* (*X*, *R* = *H*).—The above compound (2 g.) was dissolved in dry pyridine (10 c.c.) and treated with benzoyl chloride (1·5 c.c.). After shaking well for five minutes, the mixture was heated on the water-bath for ½ hour and then added to ice-water containing hydrochloric acid. The benzoyl derivative which separated as an oil was taken in ether, the ether solution washed successively with dilute hydrochloric acid, and aqueous sodium hydroxide. After a final washing with water, the solution was dried over calcium chloride and the solvent distilled. The solid product was crystallised first from alcohol, then from benzene and finally from benzene-alcohol mixture. The benzoyl derivative was thus obtained as broad rectangular plates and prisms and melted at 87–88°. Yield, 2 g. The substance gave no ferric reaction and did not dissolve in cold aqueous alkali. (Found: C, 65·6; H, 5·8; $C_{18}H_{18}O_6$ requires C, 65·5; H, 5·5%.)

2-*Hydroxy*-4 : 5 : 6-*trimethoxydibenzoylmethane* (*XI*, *R* = *H*).—To a solution of the above benzoyl derivative (2 g.) in dry toluene (30 c.c.) was added sodamide (8 g.) which had been finely powdered under toluene. The mixture was well stirred for 10 minutes and then heated on the boiling water-bath for 4 hours with frequent shaking. The yellow solid product was filtered, washed well with hot benzene, dried and carefully added to ice-cold water. The resulting yellow solution was filtered and saturated with carbon dioxide. The dibenzoylmethane separated as a deep orange-red oil which turned into a deep-yellow solid when left in the refrigerator for two days. It was collected, washed with water, dried and crystallised from benzene, light petroleum mixture. Yield, 1·2 g. After a second crystallisation from the same solvent the diketone was obtained as golden yellow rectangular

plates and prisms and melted at 99–100°. It was easily soluble in alcohol, acetone and benzene and dissolved in aqueous sodium hydroxide to a bright yellow solution. Its alcoholic solution gave a deep brownish-green colour with ferric chloride. (Found: C, 65·3; H, 5·8; $C_{18}H_{18}O_6$ requires C, 65·5; H, 5·5%.)

5 : 6 : 7-*Trimethoxy-flavone* (*Baicalein trimethyl ether, XII, R = H*).—The dibenzoylmethane (1 g.) was dissolved in glacial acetic acid (10 c.c.) and to the solution was added fused sodium acetate (2 g.). The mixture was gently boiled over a wire-gauze for 4 hours and then diluted with water (100 c.c.). When allowed to stand for two or three hours, the solution deposited a practically colourless crystalline solid which was collected, washed, and crystallised from aqueous alcohol. Yield, 0·6 g. On recrystallisation from dilute alcohol the trimethoxyflavone was obtained as colourless elongated rectangular prisms (mostly rods) and melted at 165–66° (Hattori[15] gives m.p. 163–64°). It was insoluble in aqueous sodium hydroxide and gave no colour with ferric chloride. Its solution in concentrated sulphuric acid was yellow without any fluorescence in daylight. With magnesium and concentrated hydrochloric acid its alcoholic solution developed an orange-yellow colour. (Found: C, 69·1; H, 4·9; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%.)

5 : 6 : 7-*Trihydroxy-flavone* (*Baicalein, XIII, R = H*).—The foregoing methoxy flavone (0·3 g.) was dissolved in acetic anhydride (5 c.c.) and cautiously treated with hydriodic acid (*d.* 1·7; 5 c.c.) and the mixture heated at 135–40° for two hours (oil-bath). On pouring the cooled reaction mixture into water saturated with sulphur dioxide, the trihydroxy flavone separated as an yellow solid, which was collected, boiled with water and crystallised twice from alcohol. It formed yellow coloured narrow rectangular plates and melted at 264–65° (Shibata, Iwata and Nakamura[4] give m.p. 264–65°).

The trihydroxy flavone was moderately soluble in alcohol, more so in acetone and glacial acetic acid, but sparingly soluble in petroleum ether. Its solution in concentrated sulphuric acid was deep yellow and exhibited no fluorescence. In alcoholic solution it gave an orange-yellow precipitate with lead acetate, and a brown colour with a tinge of green with ferric chloride. When added to aqueous ammonia, the crystals developed an orange-red colour and dissolved to give a bright-yellow solution. The flavone dissolved with difficulty in aqueous sodium carbonate to a greenish-yellow solution which gave a dark greenish-brown precipitate on keeping. In 10% aqueous sodium hydroxide the crystals turned deep red in colour and subsequently changed into greenish-brown flocks. When treated with

sodium amalgam in absolute alcohol, it immediately gave green flocks (Bargellini's test). (Found: C, 66·6; H, 4·0; $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%.)

Baicalein triacetate.—The triacetate was prepared by treating the flavone (0·1 g.) with acetic anhydride (5 c.c.) and fused sodium acetate (1 g.) and boiling the mixture for two hours. When crystallised twice from ethyl acetate, it was obtained as short, colourless rectangular rods and it melted at 194–95° with slight sintering at 190° (Shibata, Iwata and Nakamura[4] give m.p. 191–92°).

2 - *Anisoyloxy* - 4 : 5 : 6 - *trimethoxyacetophenone* (*X*, $R = OCH_3$).—2-Hydroxy-4 : 5 : 6-trimethoxyacetophenone (IX) (2 g.) was anisoylated by heating with anisoyl chloride (2 c.c.) and dry pyridine (10 c.c.), for ½ hour on the boiling water-bath and the product worked up as in the case of the benzoyl derivative. The colourless crystalline solid, obtained on removal of the ether, was crystallised from alcohol, benzene and finally from benzene-light petroleum mixture. The anisate was thus obtained as (colourless) stout prisms and it melted at 112–13°. It did not dissolve in cold aqueous sodium hydroxide and gave no ferric reaction. (Found: C, 63·3; H, 5·2; $C_{19}H_{20}O_7$ requires C 63·3; H, 5·6%).

2-*Hydroxy*-4 : 5 : 6 : 4′-*tetramethoxydibenzoylmethane* (*XI*, $R = OCH_3$).—A solution of the above *O*-anisoyl derivative (2 g.) in dry toluene (30 c.c.) was treated with finely powdered sodamide (8 g.). The mixture which rapidly turned yellow was heated on the boiling water-bath for 5 hours and the yellow solid collected, washed with hot benzene, dried and added to ice-water. The yellow solution was saturated with carbon dioxide and the dibenzoylmethane which first separated as an oil, solidified on leaving in the refrigerator for two days. The solid was then collected, dried and crystallised from benzene-light petroleum mixture when it was obtained as bright yellow rectangular prisms melting at 114–15°. Yield, 1·2 g. It was readily soluble in alcohol, acetone and benzene but less so in petroleum ether. It dissolved in aqueous alkali to give a bright yellow solution and gave an olive green colour with ferric chloride in alcoholic solution. (Found: C, 63·5; H, 5·9; $C_{19}H_{20}O_7$ requires C, 63·3; H, 5·6%.)

5 : 6 : 7 : 4′-*Tetramethoxy flavone* (*Scutellarein tetramethyl ether*) (*XII*, $R = OCH_3$).—A mixture of the above dibenzoylmethane (1 g.), glacial acetic acid (10 c.c.) and fused sodium acetate (2 g.) was gently boiled for 4 hours and diluted with water (100 c.c.). The aqueous solution was extracted with ether and the ether solution carefully shaken with 5% aqueous sodium carbonate to remove acetic acid and then washed with water. On

distillating off the solvent, a colourless crystalline solid was obtained which was recrystallised from dilute alcohol. Yield, 0·8 g. It was readily soluble in the common organic solvents and on recrystallisation from aqueous alcohol, scutellarein tetramethylether was obtained as colourless stout cubical crystals and melted at 162–63° (Goldschmiedt and Zerner[2] give m.p. 158–60°). It was insoluble in aqueous alkali and gave no colour with ferric chloride in alcoholic solution. It dissolved in concentrated sulphuric acid to give an yellow solution which exhibited no fluorescence. (Found in a sample dried *in vacuo* at 130° for two hours; C, 66·8; H, 5·5; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%.)

5:6:7:4′-*Tetra-hydroxy flavone* (*Scutellarein, XIII, R* = *OH*).—The demethylation of the tetramethoxy flavone (0·2 g.) was effected by heating (oil-bath) at 135–40° with acetic anhydride (5 c.c.) and hydriodic acid (*d*, 1·7; 5 c.c.). The tetrahydroxy flavone was twice crystallised from alcohol when it was obtained as short, yellow needles. Yield, 0·15 g. It turned brown at about 300° and did not melt down below 340° (Goldschmiedt and Zerner[2] found that it becomes dark at about 300° and does not melt or decompose below 330°). The substance dissolved in alcohol, acetone and ethyl acetate with difficulty but more readily in glacial acetic acid. Its solution in concentrated sulphuric acid was yellow without any fluorescence. With lead acetate in alcoholic solution it gave an orange yellow precipitate and with ferric chloride it developed a green colour which turned brown with a tinge of green. The substance dissolved in ammonia to give a bright yellow solution which subsequntly turned orange-brown; in aqueous sodium carbonate it gave an yellow colour which rapidly turned green. In aqueous sodium hydroxide it formed a deep greenish-yellow solution which immediately became pure green in colour; no precipitate was obtained even on keeping the solution for 24 hours. When the substance was treated with sodium amalgam in absolute alcohol, there was an immediate formation of green flocks (Bargellini's test). (Found: C, 63·0; H, 3·8; $C_{15}H_{10}O_6$ requires C, 62·9; H, 3·5%.)

Scutellarein tetraacetate.—The tetraacetate prepared by heating (oil-bath) the hydroxy flavone (0·1 g.) with acetic anhydride (5 c.c.) and fused sodium acetate (1 g.) was crystallised twice from acetic acid-alcohol mixture. It was obtained as long fine needles and melted at 240–41° (Goldschmiedt and Zerner[2] give m.p. 235–37°; Wessely and Moser[8] give m.p. 238°).

Summary

A simple and at the same time unambiguous method of synthesis of the 5:6:7-hydroxyflavones, baicalein and scutellarein and their derivatives is

described. It starts from phloracetophenone which is partially methylated to the 4:6-dimethyl ether. Oxidation of this ether with potassium persulphate yields the 2:5-dihydroxy compound which on partial methylation produces 2-hydroxy-4:5:6-trimethoxyacetophenone. Using the benzoyl and anisoyl derivatives of this ketone and adopting the Baker-Venkataraman procedure, the trimethyl ether of baicalein and the tetramethyl ether of scutellarein have been prepared and from them the hydroxyflavones and their acetates.

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SYNTHESIS OF 5:6:7-HYDROXYFLAVONES AND THEIR DERIVATIVES—PART II

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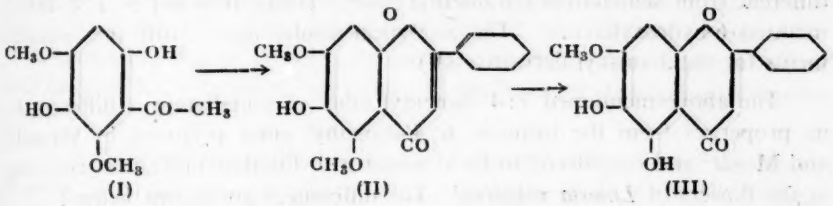
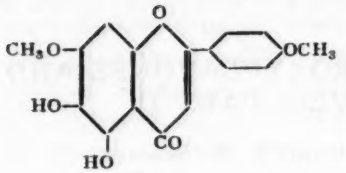
In continuation of the work described in Part I,[1] an attempt has been made to prepare partially methylated derivatives of baicalein and scutellarein. For this purpose 2:5-dihydroxy-4:6-dimethoxy acetophenone (I) is subjected to the Allan-Robinson condensation using the anhydride and sodium salt of (1) benzoic acid and of (2) anisic acid. In the first case the product is 5:7-dimethoxy-6-hydroxyflavone (II). On methylation it yields 5:6:7-trimethoxy flavone, baicalein-trimethyl ether, identical with the sample prepared by the Baker-Venkataraman method.[1] Partial demethylation could be effected using aluminium chloride under mild conditions yielding 7-methoxy-5:6-dihydroxyflavone (baicalein-7-methyl ether III).

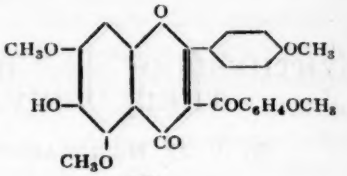


In its properties and reactions it is markedly different from oroxylin-A[2] which is considered to be the 6-methyl ether of baicalein. The mixed melting point with a sample of the latter obtained from the root bark of ***Oroxylum indicum*** is depressed. The comparison is brought out in the following table:

	Oroxylin-A	7-Methyl ether of Baicalein
Appearance ..	Yellow needles	Thick rhombohedral prisms (Yellow)
M.p. of the substance ..	230–31°	219–20°
,, acetate ..	131–32°	239–40°
Alcoholic $FeCl_3$ ..	Red-violet	Green
Aq. NaOH ..	Yellow solution	Greenish-brown precipitate
Na Amalgam ..	Yellow solution	Blue solution, and a brown precipitate after an interval



(IV)



(V)

The condensation of the above dihydroxy ketone (I) with anisic anhydride and sodium anisate gives rise to two products which could be separated by fractional crystallisation from alcohol. The less soluble component is a dimethyl ether whose colour reactions are very similar to those of the 7-methyl ether of baicalein. On methylation it yields the tetra-methyl ether of scutellarein and hence it is considered to be the 7: 4′-dimethyl ether of scutellarein (IV). Its formation should be due to partial demethylation taking place during the Allan-Robinson condensation. Such demethylation has been noted in many other similar cases.

The second product obtained in very poor yields resembles in its reactions 5: 7-dimethoxy-6-hydroxyflavone (II). Its methyl ether is, however, different from scutellarein tetramethyl ether. Hence it is not 5: 7: 4′-tetramethoxy-6-hydroxyflavone. The analytical results agree with the requirements for the 3-anisoyl derivative (V).

The above mentioned 7: 4′-dimethyl ether of scutellarein is different in its properties from the isomeric 6: 4′-dimethyl ether prepared by Wessely and Moser[3] and considered to be identical with the dimethyl ether occurring in the flowers of *Linaria vulgaris*.[4] The differences are shown below:

	7 : 4′-dimethyl ether of scutellarein	6 : 4′-dimethyl ether
Appearance ..	Yellow rectangular plates	Fine yellow needles
Melting point ..	211–12°	201°, 219°
Aq. NaOH ..	Slowly forms a greenish yellow solution and a greenish brown precipitate is deposited	Yellow solution
$FeCl_3$ reaction ..	Stable green	Dark brown

Experimental

5: 7-*Dimethoxy-6-hydroxyflavone* (II).—2: 5-Dihydroxy-4: 6-dimethoxyacetophenone (1 g.), benzoic anhydride (5 g.) and sodium benzoate (2 g.) were intimately mixed and heated under diminished pressure at 180–85° (oil-bath) for 4 hours. After cooling, the hard brown mass was broken up, alcohol (50 c.c.) added and the mixture refluxed on the water-bath for 10

minutes. A solution of potassium hydroxide (4 g.) in water (6 c.c.) was then gradually introduced during the course of 15 minutes and the refluxing continued for a further 20 minutes. After distilling the alcohol under reduced pressure, the greenish-brown residue was dissolved in water (100 c.c.) and the solution filtered to remove any insoluble matter. On saturating it with carbon dioxide, the crude flavone separated as a brown solid which was filtered and crystallised twice from alcohol (animal charcoal). Yield 0·2 g. By another crystallisation from the same solvent, the dimethoxyflavone was obtained as pale yellow thick cubical crystals whereas it came down as fine needles when quickly crystallised. It melted at 212–13° and a further crystallisation did not raise the melting point.

It was moderately soluble in alcohol and more easily in acetone and glacial acetic acid. It dissolved in aqueous sodium hydroxide to give a bright a yellow solution. In alcoholic solution it gave a weak brown colouration with ferric chloride and its solution in concentrated sulphuric acid was yellow without any fluorescence in daylight. (Found: C, 68·6; H, 4·9; $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%.)

The substance (0·1 g.) was acetylated by refluxing (oil-bath) with acetic anhydride (5 c.c.) and fused sodium acetate (1 g.) for 3 hours. The acetate was crystallised from dilute acetic acid when it was obtained as colourless stout plates melting at 218-19°. It did not dissolve in cold aqueous alkali and gave no ferric reaction. (Found: C, 66·9; H, 4·9; $C_{19}H_{16}O_6$ requires C, 67·1; H, 4·7%.)

5 : 6 : 7-*Trimethoxyflavone* (*Baicalein trimethyl ether*).—The dimethoxy flavone (0·15 g.) was methylated in dry acetone (25 c.c.) using anhydrous potassium carbonate (2 g.) and dimethyl sulphate (1 c.c.) and boiling for 12 hours. The crude methyl ether separated as a practically colourless crystalline solid and it crystallised from dilute alcohol as colourless elongated rectangular prisms, melting at 165-66°. It was identical with baicalein trimethyl ether already reported[1] and the mixed melting point was undepressed. (Found: C, 68·9; H, 5·4; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%.)

7-*Methoxy*-5 : *O-dihydroxyflavone* (*7-O-methyl baicalein*).—The partial demethylation of the above dimethyl ether (II) had to be effected under carefully controlled conditions. Excess of aluminium chloride and high temperature resulted in the reaction going too far producing baicalein.

To a solution of the dimethoxyflavone (0·25 g.) in nitrobenzene (25 c.c.) was added finely powdered anhydrous aluminium chloride (0·5 g.) and the mixture kept at the laboratory temperature for 24 hours. On the addition of petroleum ether, a yellow solid was precipitated, which was collected and

washed with a further quantity of petroleum ether to remove adhering nitrobenzene. The solid was added to water (50 c.c.) containing concentrated hydrochloric acid (2 c.c.) and glacial acetic acid (5 c.c.) and the mixture heated on the boiling water-bath for 15 minutes. The solution was then cooled and further diluted with water when the 7-methyl ether separated as an yellow crystalline solid. It was filtered, washed and crystallised twice from alcohol. Yield 0·15 g. On recrystallisation from absolute alcohol, it was obtained as thick rhombohedral prisms and melted at 219–20°. The melting point was depressed on admixture with an equal quantity of oroxylin-A. The dihydroxyflavone was moderately soluble in alcohol and acetone, and gave a stable green colouration with ferric chloride in alcoholic solution. With aqueous sodium hydroxide the crystals developed an orange-red colour and then changed into a dark greenish-brown precipitate. On treatment with sodium amalgum in absolute alcohol (Bargellini's test), the dihydroxyflavone gave an orange yellow solution which rapidly changed through green to blue in colour; a brown precipitate was obtained after some time. With lead acetate in alcoholic solution it gave an orange yellow precipitate. The yellow solution in concentrated sulphuric acid exhibited no fluorescence. (Found: C, 67·5; H, 4·4; OCH_3, 10·3; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·3; OCH_3, 10·9%.)

The dihydroxyflavone (0·1 g.) was acetylated by refluxing (oil-bath) with acetic anhydride (5 c.c.) and sodium acetate (1 g.) for two hours. The diacetate was crystallised twice from ethyl acetate when it was obtained as shining elongated hexagonal plates melting at 239–40°. (Found: C, 65·1; H, 4·6; $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·3%.)

5:6-*Dihydroxy*-7: 4′-*dimethoxyflavone* (7: 4′-*O*-*dimethyl scutellarein*).—An intimate mixture of the dihydroxyacetophenone (I, 2 g.), anisic anhydride (12 g.) and sodium anisate (4 g.) was heated under diminished pressure at 180–85° (oil-bath) for 6 hours. The hydrolysis was effected by refluxing with alcohol (100 c.c.) and a solution of potassium hydroxide (10 g.) in water (10 c.c.) and the product worked up in the usual manner. The crude product obtained on saturating the alkaline solution with carbon dioxide was filtered and washed with water. Yield, 0·25 g. It gave two fractions on crystallisation from alcohol. When the hot alcoholic solution was cooled, a sparingly soluble yellow solid first separated. It was collected and crystallised twice from the same solvent when 5:6-dihydroxy-7:4′-dimethoxyflavone was obtained as yellow rectangular plates, melting at 211–13° with sintering at 208°. Yield, 0·15 g. Further crystallisation did not raise the melting point. The substance was moderately soluble in acetone but not so

readily in alcohol. Its solution in concentrated sulphuric acid was yellow and exhibited no fluorescence. In alcoholic solution it gave a stable green colouration with ferric chloride. When treated with dilute aqueous sodium hydroxide, the substance first became orange-red, then turned into greenish-blue flakes and dissolved to give a greenish-yellow solution; on allowing to stand, a greenish-brown precipitate was subsequently deposited. (Found: C, 65·0; H, 4·7; OCH_3, 19·0; $C_{17}H_{14}O_5$ requires C, 65·0; H, 4·5; OCH_3, 19·7%.)

The dihydroxyflavone (0·1 g.) was methylated using dry acetone (30 c.c.), anhydrous potassium carbonate (1 g.) and acid-free dimethyl sulphate (0·5 c.c.). The methyl ether was crystallised from dilute alcohol when it was obtained as colourless stout cubical crystals melting at 161-62° and identical with scutellarein tetramethyl ether.

5 : 7 : 4′-*trimethoxy*-6-*hydroxy*-3-*anisoyl-flavone*.—The alcoholic mother-liquor obtained after filtering off the above compound, was concentrated and allowed to cool. A pale greenish-yellow solid separated which after two crystallisations from dilute alcohol came out as pale yellow narrow rectangular plates and melted at 224-26°. Yield, 75 mg. It dissolved in aqueous sodium hydroxide to give an yellow solution. Its solution in alcohol gave a weak brown colouration with ferric chloride. (Found: C, 67·7; H, 4·9; OCH_3, 26·4; $C_{26}H_{22}O_8$ requires C, 67·5; H, 4·7; OCH_3, 26·8%.)

Summary

Employing 2 : 5-dihydroxy-4 : 6-dimethoxyacetophenone and the Allan-Robinson method, the 5 : 7-dimethyl ether of baicalein is obtained and from it by partial demethylation the 7-methyl ether. This is definitely different from oroxylin-A. The use of anisic anhydride in the above condensation yields two products, (1) 7 : 4′-dimethyl ether of scutellarein and (2) 5 : 7 : 4′-trimethyl ether of 3-anisoyl-scutellarein. The former is different from the 6 : 4′-dimethyl ether obtained from natural sources.

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SYNTHETICAL EXPERIMENTS IN THE CHROMONE GROUP

Part XX. A New Synthesis of 5 : 6 Dihydroxyflavone

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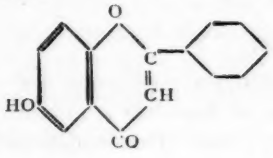
Examining the reactivity of natural colouring matters derived from phloroglucinol towards diazo salts, A. G. Perkin[1] found that chrysin, apigenin, euxanthone and catechin gave *dis*azo dyes. Mahal and one of us[2] have shown that 6-hydroxyflavone (I) couples with diazotised *p*-nitraniline to form a mono-azo dye, formulated as (II) in view of the stabilisation of one of the Kekule forms of the benzene ring in chromone due to fusion with the γ-pyrone ring, as indicated in (I). It was suggested[2, 3] that a route to the synthesis of 5:6-dihydroxyflavone (III) thus becomes possible. We have now confirmed that 6-hydroxyflavone couples with diazo salts in the 5-position, and have synthesised 5:6-dihydroxyflavone by a method which promises to be of value for the synthesis of other di- and polyhydroxyflavones and flavonols.



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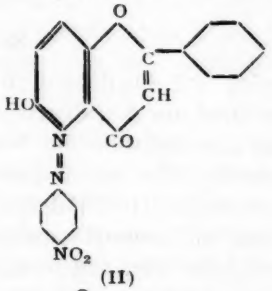

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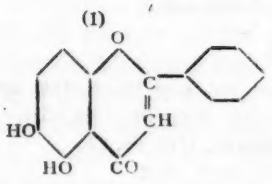

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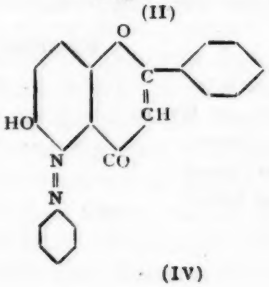

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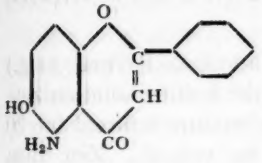
Coupling diazobenzene chloride with 6-hydroxyflavone (I), dissolved in alcohol-pyridine with the addition of ammonia, a nearly quantitative yield of 5-benzeneazo-6-hydroxyflavone (IV) was obtained. 6-Hydroxyflavone is sparingly soluble in aqueous caustic soda, and the sodium salt tends to separate at the low temperature necessary for coupling, although diazotised *p*-nitraniline on account of its greater coupling energy in comparison with diazobenzene chloride couples readily with the flavone even under these conditions. The dye (IV) was reduced to 5-amino-6-hydroxyflavone (V) by means of zinc dust in boiling acetic acid. Other reagents for this reduction, as well as the hydrosulphite reduction of the alkali-soluble azo dye obtained by coupling diazotised sulphanilic acid with 6-hydroxy-



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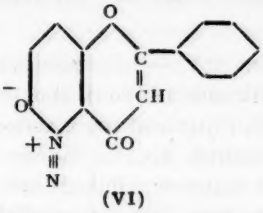

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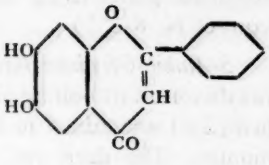

(VII)

flavone, were tried, but various difficulties were encountered in the isolation of the aminohydroxyflavone; and the zinc-acetic acid procedure was found to be the most suitable.

When the amine (V) was dissolved in hydrochloric acid and treated with sodium nitrite, the brownish yellow product crystallised from alcohol in needles, which were insoluble in aqueous alkali, gave a yellow solution in concentrated sulphuric acid, gave no colouration with ferric chloride and decomposed on heating at about 173°. From these reactions and the nitrogen content, the substance is regarded as the diazo oxide (VI).[4] Boiled with 50% sulphuric acid, the diazo oxide (VI) underwent hydrolysis, and gave a dihydroxyflavone, which agreed in all its properties, including the m.p. of the diacetyl derivative, with the 5:6- (III), and not with the 6:7-isomer (VII). 6:7-Dihydroxyflavone (VII) has been synthesised by Chadha and one of us[5] by the Robinson reaction on 2:4:5-trihydroxyacetophenone; and 5:6-dihydroxyflavone by Baker[6] by the action of sodamide[7] on 2-benzoyloxy-5:6-dimethoxyacetophenone, followed by cyclicisation and demethylation. Nakazawa[8] has synthesised 5:6-dihydroxyflavone by a route very similar to Baker's; 2-hydroxy-6-methoxyacetophenone was oxidised to 2:5-dihydroxy-6-methoxyacetophenone, the dibenzoate of which was converted to the β-diketone by the sodamide method[7]; cyclicisation and hydrolysis gave 5-methoxy-6-hydroxyflavone, which was demethylated[9] by means of aluminium chloride in nitrobenzene to 5:6-dihydroxyflavone (III).

Experimental

5-Benzeneazo-6-hydroxyflavone (IV).—A solution of diazobenzene chloride, prepared from aniline (2 g.; 2·5 mol.), concentrated hydrochloric acid (6 c.c.), alcohol (30 c.c.) and sodium nitrite (1·8 g. in 10 c.c. water), was gradually added at 0° to a solution of 6-hydroxyflavone (2 g.) in alcohol (50 c.c.), pyridine (14 c.c.) and ammonia (*d.* 0·88; 2 c.c.). During addition of the diazo solution and for six hours thereafter, the mixture was mechanically stirred and maintained at 0·5°. On leaving overnight, the dark red precipitate was collected, boiled with hot 50% hydrochloric acid for a few minutes, filtered, washed, and crystallised from alcohol. The dark red, elongated plates (2 g.) melted at 191–92°. (Found: N, 8·4. $C_{21}H_{14}O_2N_2$ requires N, 8·2%.)

5-Amino-6-hydroxyflavone (V).—5-Benzeneazo-6-hydroxyflavone (1 g.) was dissolved in boiling acetic acid (30 c.c.), and to the boiling solution zinc dust (2 g.) was added in small lots and the reaction mixture refluxed for 20 minutes. The deep red solution became brown in colour. Zinc dust (0·5 g.) was added, and the solution refluxed for 20 minutes longer. The solution was filtered and the zinc dust extracted thrice with 5 c.c. portions of hot acetic acid. The filtrate was cooled, diluted with water and allowed to stand in the refrigerator. The yellowish brown precipitate was filtered, washed with water, sucked dry, and dissolved in hot alcohol (Norit). The filtered alcoholic solution was diluted with water and allowed to stand in the refrigerator. The orange-brown clusters of needles were collected and dried *in vacuo*. The substance (0·5 g.) melted at 235° after shrinking at 200° (Found: N, 5·7. $C_{15}H_{11}O_2N$ requires N, 5·5%.) The brown alcoholic solution turns dark greenish brown on the addition of ferric chloride. The substance dissolves in caustic soda giving an orange brown colour. It gives a pale brown colour with concentrated sulphuric acid. It gradually goes into a pale brown solution by boiling with N-hydrochloric acid.

Flavone-5-diazo-6-oxide (VI).—5-Amino-6-hydroxyflavone (0·5 g.) was boiled with N-hydrochloric acid (20 c.c.), till most of it went into solution. The solution was filtered, and the residue twice extracted with 20 c.c. portions of the acid. A small amount of undissolved resinous matter was rejected. The combined hydrochloric acid extracts were cooled to room temperature and sodium nitrite (2 g.) was added in small lots, the reaction flask being rotated during addition. On leaving the reaction mixture in the refrigerator for 30 minutes, the yellowish brown precipitate was filtered, washed with water and dried. There was no appreciable change in the yield by carrying out the sodium nitrite addition at 10° or 50°. Crystallised from alcohol,

glistening brown needles were obtained, which decomposed at 173°. (Found: C, 68·2; H, 3·1; N, 10·4. $C_{15}H_8O_3N_2$ requires C, 68·2; H, 3·0; N, 10·6%.) The substance does not respond to Lassaigne's sodium fusion test for nitrogen. It is insoluble in aqueous caustic soda, and dissolves in concentrated sulphuric acid with a yellow colour. The alcoholic solution gives no colouration with ferric chloride. The method of preparation, the colour of the substance, its instability to heat and other properties are characteristic of the diazo oxides.[4]

5:6-*Dihydroxyflavones* (III).—To a boiling mixture of concentrated sulphuric acid (10 c.c.) and water (10 c.c.) the flavone diazo oxide (VI) (0·1 g.) was added in small lots. It immediately went into solution with frothing, a reddish brown solution being formed. Boiling was continued for five more minutes, the solution allowed to cool, and diluted with water. On letting stand in the refrigerator, the yellowish brown precipitate was filtered, washed free from acid, and twice crystallised from dilute alcohol. The honey-yellow needles (0·03 g.) melted at 189-90° (Found: C, 70·9; H, 4·3. $C_{15}H_{10}O_4$ requires C, 70·8; H, 3·9%). The alcoholic solution of the substance gives an intense olive green colour with ferric chloride; an orange red precipitate with lead acetate in alcohol; and a red insoluble sodium salt when aqueous sodium hydroxide is added. The yellow solution in concentrated sulphuric acid exhibits no fluorescence.

5:6-*Diacetoxyflavone*.—5:6-Dihydroxyflavone (0·05 g.) was dissolved in acetic anhydride (2 c.c.) and fused sodium acetate (0·5 g.) added. The mixture was refluxed for 2 hours, poured over crushed ice, the greyish brown solid collected, washed with water and crystallised from alcohol (Norit). The pale yellow prisms melted at 164-65° (Found: C, 67·8; H, 4·3. $C_{19}H_{14}O_6$ requires C, 67·4; H, 4·2%).

While the properties of our dihydroxyflavone agree with those recorded for 5:6-dihydroxyflavone, the following table gives a comparison of the properties of 5:6-dihydroxyflavone[6] and 6:7-dihydroxyflavone.[5] The latter would have been obtained if the coupling of 6-hydroxyflavone with diazobenzene chloride had taken place in the 7- instead of the 5-position.

Properties	5 : 6–Dihydroxyflavone	6 : 7–Dihydroxyflavone
Crystalline form	Honey-yellow needles	Pale creeam coloured silky needles
M.P.	189–90°	254°
Ferric chloride	Intense olive green	Intense green
Concentrated sulphuric acid	Yellow non-fluorescent solution	Colourless non-fluorescent solution
Aqueous sodium hydroxide	Red insoluble sodium salt	Bright yellow solution
Alcoholic lead acetate	Orange red precipitate	Greenish yellow precipitate
Diacetyl derivative	Prisms, m.p. 164–65°	Needles, m.p. 201°

Summary

It has been shown that 6-hydroxyflavone couples with diazo salts in the 5-position. 5-Benzeneazo-6-hydroxyflavone has been reduced to 5-amino-6-hydroxyflavone. Treatment of the latter with nitrous acid gave flavone-5-diazo-6-oxide, hydrolysis of which with boiling dilute sulphuric acid led to 5:6-dihydroxyflavone.

The utility of the general procedure for the synthesis of other poly-hydroxyflavones and methoxyhydroxyflavones is being studied.

We are indebted to the Sir Dorab Tata Trust for a Research Fellowship awarded to one of us.

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THE GLYCERIDE COMPOSITION OF FATS AND OILS

Part II. The Fatty Acids and Glycerides of *Terminalia belerica* (Roxb.)

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Oils of *Terminalia* genus have been little investigated. Of the three more important species *Terminalia catappa*[1, 2] (Indian almond), *Terminalia chebula*[3] and *Terminalia belerica*,[4] only the first has been examined by the ester fractionation method; the oil from *Terminalia chebula* has merely been separated into saturated and unsaturated acids while *Terminalia belerica* oil does not seem to have been investigated in detail at all. No member of this genus has been investigated with regard to the glyceride structure till now.

The first examination of oil of *Terminalia belerica* seems to have been made by Hefter[5] who, however, has reported only that the seed kernel yields 44% of a fatty oil which consists of solid and liquid glycerides. Hooper[6] has recorded some constants of two specimens of the oil. We have now examined two specimens of the oil for component acids, one by ester fractionation procedure and the other by the simple but equally accurate Bertram procedure. The component acids consist of palmitic and stearic with a little arachidic in the saturated series and probably only oleic and linoleic acids in the unsaturated class. All the three species of *Terminalia* are characterised by the presence of about 25% of linoleic acid (see below). *Terminalia catappa* and *Terminalia belerica* show a closer resemblance in

	Weight percentage on total acids					
	Saturated				Unsaturated	
	C·14	C·16	C·18	C·20	Oleic	Linoleic
T. catappa—1 ..	1·0	29·0	4·1	0·8	41·7	23·4
2 ..	..	34·0	9·7	0·4	27·3	28·6
T. chebula ..	..	17·8	..	..	58·8	23·4
T belerica :						
Ester method ..	..	22·4	15·7	0·8	28·1	33·0
Bertram method ..	..	20·5	20·8	..	26·7	32·0

the large amount of saturated acids which they contain, though those of the latter consist principally of palmitic acid while those of the latter consist of about an equal mixture of palmitic and stearic.

We have completed the examination of one specimen of *T. belerica* oil (I.V. 78·5; Saturated acids 41·3%) for the constituent glycerides according to the oxidative method evolved in our laboratory.[8, 10] The absence of fully saturated glycerides in any quantity was proved by a preliminary oxidation which gave only 0·0018 gram of neutral material from 6 grams of the oil. The mean molecular weight of the saturated acids was found to be 270·0 and 270·2 in two separate determinations, their percentages being 39·49 and 39·5 on the weight of the oil. Since fully saturated components were absent, washing of the ethereal solution of the acidic oxidation products leaves behind monoazelao-disaturated glycerides and diazelao-monosaturated glycerides together with any unoxidised fat. The results of two typical examinations are detailed in the experimental section.

As shown in the experimental part, the percentage composition by weight of the component acids of the above specimen of *Terminalia belerica* oil is palmitic 20·50, stearic 20·80, oleic 26·70 and linoleic 32·0; which, as expressed by molecules, is palmitic 22·2, stearic 20·2, oleic 26·1 and linoleic 31·5; thus making a total of 42·4 molecules of saturated acids and 57·6 molecules of unsaturated acids. Of this, 18·6 molecules of saturated acids are combined as GS_2U and none as GS_3, hence the remaining 23·8 molecules are combined as GSU_2, thus forming 71·4 molecules of di-oleo-monosaturated glycerides and the final composition of the oil is: GS_3 traces, GS_2U 28%, GSU_2 71·4% and GU_3 0·6%. The glyceride composition as calculated by some methods of partitioning of the fatty acids among themselves[7] are shown in the accompanying table:

	GS_3	GS_2U	GSU_2	GU_3
Determined ..	Trace	28·0	71·4	0·6
Even distribution ..	0	27·3	71·7	0
Oleic among others ..	12·4	45·0	..	42·6
Linoleic among others ..	3·2	58·8	..	38·0
Oleic among others, then excess of linoleic over oleo dilinolene among saturated	..	59·9	7·4	32·7

The most striking aspect about the glyceride constitution of oil of *Terminalia belerica* is its close approximation to the rule of even distribution which is not met with in many of the other seed fats which we have examined so far. It would, at this point, be of interest to compare the glyceride

composition of a Mowra oil, which we have recently investigated[8] and which had practically the same saturated-unsaturated acid ratio. The component acids are the same and there is not much difference in their proportions except in the relative proportions of oleic and linoleic acids. But the glyceride structure is entirely different in the two cases. This shows that probably the general mode of construction or assembling of the acids into triglycerides need not be the same even in any two vegetable seed fats (compare Hilditch[9]).

Experimental

Weight of oil oxidised	..	5·3788 grams
Weight of azelao glyceride mixture after washing with bicarbonate	..	3·1475 ,,
Saponification value of the mixture	..	359·1
Weight of recovered total saturated fatty acids	..	2·1450 ,,
Iodine value of recovered saturated acids	..	0·90

The iodine value 0·9 of the acids recovered corresponds to the unoxidised portion of the oil. After Bertram separation, the weight of acids is 2·145 grams, which works up to, on the weight of oil, 2·145 × 100/5·3788 or 39·87%. The percentage of unsaturated unoxidised acid will be 0·9 × 39·87/90 or 0·398 on the weight of oil (90 being the iodine value of oleic acid). Since, for purposes of computation, the percentage of unsaturated glycerides (unoxidised) will be approximately thrice the unsaturated acids, the percentage of unoxidised unsaturated glycerides is 0·398 × 3 or 1·2.

A more detailed calculation is as follows :—

282 of oleic acid should give [282 + (2 × 270) + 38] of GS_2U by weight when S is 270 (mean molecular weight in the present instance[2]) or 860. Here the assumption is that of the two mixed unsaturated glycerides (GS_2U and GSU_2) the GS_2U has greater probability of escaping complete oxidation.

The weight per cent. of GS_2U will be 0·398 × 860/282 or 1·205 per cent. 1·2 per cent. of the oil is contained in 3·1475 grams of the azelao glyceride mixture obtained experimentally. Hence the percentage content of unoxidised oil based on the azelao-glycerides mixture will be

$$1·2 \times 5·3788/3·1475 \text{ or } 2·05.$$

The saponification value of 2·05% will be 56·11 × 100 × 3/860 or 195·7. Hence the S. V. of the mono-, and diazelao-glyceride mixture can be calculated. The actual experimental saponification value of the mixture containing GS_3, GS_2U, GS_2A and GSA_2 is 359·1. In this case of course, GS_3 is nil and hence we have now to correct for the saponification value of GS_2U.

If X is the saponification value of the mixture, GS_2A and GSA_2, then $359{\cdot}1 \times 100 = 195{\cdot}7 \times 2{\cdot}05 + (X \times 97{\cdot}95)$, where 97·95 is the sum total of the percentage of GS_2A and GSA_2. Hence X is 362·3.

Weight of mixture of azelao-glycerides is $3{\cdot}1475 \times 97{\cdot}95/100$. The percentage weight of mono-azelao-glycerides is

$$\frac{3{\cdot}1475 \times 97{\cdot}95 \times (410{\cdot}2 - 362{\cdot}3)}{100 \times 5{\cdot}3788\,(410{\cdot}2 - 293)} \times 100 \text{ or } 23{\cdot}42,$$

since saponification value of GS_2A is 293·0 and of GSA_2 is 410·2 (experimental determination gave 410·8) and percentage of GSU_2 by weight is $23{\cdot}4 \times 860{\cdot}2/766{\cdot}2$, 1·2 or 27·5.

In a duplicate experiment 4·4739 grams of oil were oxidised and 2·6020 grams of azelao-glyceride mixture was obtained after washing with bicarbonate. The mixture of glycerides had a saponification value of 358·4. After Bertram separation, the saturated acids obtained weighed 1·7778 grams. The recovered saturated acids had an iodine value of 0·6. Hence percentage of unoxidised fat as oleo disaturated glycerides is 0·8, and percentage of unoxidised fat in azelao-glyceride mixture is 1·4. The percentage weight of azelao-glycerides is $58{\cdot}16 \times 98{\cdot}6/100$. True saponification value of azelao-glycerides is 360·6. Hence percentage weight of monoazelao-glycerides is

$58{\cdot}16 \times 86{\cdot}6/100 \times 49{\cdot}6/117{\cdot}2$ or 24·27.

Percentage of GS_2U by weight is $24{\cdot}27 \times 860{\cdot}2/766{\cdot}2$, 0·8 or 28·0.

Percentage of GS_2U in oil by weight is 27·5, 28·0/2, or 27·75.

Percentage of GS_2U in oil by molecules is 28·0.

Analysis of the Oil by Ester Fractionation—1941 *Sample.*—187 grams of the seed kernel was exhausted with benzene yielding 74·4 grams of the oil corresponding to an yield of 39·8%. 218 grams of the oil was hydrolysed yielding 203 grams of mixed acids of mean molecular weight 277·8; iodine value 87·36; Titre 35; Refractive index (40) 1·4524.

The mixed acids separated into solid and liquid acids by lead salt separation yielded, approximately, 75·2 grams of solid acids and 127·8 grams of liquid acids. They gave the following analytical constants:—

	Solid Acids	Liquid Acids
Refractive Index ..	1·4434 (60)	1·4588
Mean Molecular weight ..	272·6	281·2
Iodine Value ..	1·8	129·4

100 grams of the solid and liquid acids were separately esterified and fractionated. The solid acids fraction consisted of C_{16}—19·93; C_{18}—15·76; C_{20}—0·79; oleic—0·20; linoleic—0·32. The liquid acids fraction consisted of C_{16}—2·45; oleic—27·90 and linoleic—32·64. Hence the components are C_{16}—22·38; C_{18}—15·76; C_{20}—0·79; oleic 28·10 and linoleic 32·96 per cent.

Distillation of Solid and Liquid Acid Esters

No.	Weight	Temperature	S. Equivalent	Refractive Index	Iodine Value
			(*a*) Solid acids		
1	31·48	190–195	293·80	1·4390	0·35
2	29·15	190–195	294·50	1·4390	0·44
3	12·45	195–205	302·20	1·4410	3·85
4	6·27	Residue	318·50	1·4625	14·50
			(*b*) Liquid acids		
1	39·04	200–205	306·4	1·4505	119·7
2	32·23	205–210	309·2	1·4507	123·7
3	20·25	210–215	308·8	1·4510	125·2
4	11·34	Residue	..	1·4624	118·2

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RAMAN SPECTRA OF THE SECOND ORDER IN CRYSTALS

Part IV. Barytes

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1. Introduction

Although large transparent single crystals of barytes are easily available, comparatively little work has so far been done on its Raman spectrum. Nisi (1929) and Krishnamurti (1930) who were the early investigators on this subject recorded only a couple of Raman lines. Using the 2536·5 λ mercury radiation as exciter, Rasetti (1932) recorded a spectrum with a specimen of barytes which exhibited as many as eight low frequency lines and eight lines due to the SO_4 ion with frequency shifts 56·8, 62·2, 73·6, 88·3, 97·8, 127·3, 150·4, 189·8, 451·4, 462·2, 631·1, 647·5, 989·3, 1104·6, 1141·4 and 1167·2 cm.$^{-1}$ Using the same technique and giving longer exposures Roop Kishore (1942) repeated the experiment. Owing to the smaller dispersion of the spectrograph used by him, the number of Raman lines identified was less than that reported earlier by Rasetti. Roop Kishore, however, succeeded in recording an additional fainter line at 1088 cm.$^{-1}$ and a weak band extending from 1200 cm.$^{-1}$ to 1300 cm.$^{-1}$ He found that the orientation of the crystal with reference to the direction of illumination and observation had a marked influence on the relative intensities of the lines.

Using the 4046 and 4358 λ radiations of the mercury arc Balakrishnan (1941) investigated the effect of crystal orientation on the Raman lines due to the internal oscillations of the SO_4 ion in barytes. The specimen employed by him was in the form of a parallelepiped with its faces parallel to the cleavage planes (001), (110) and (1$\bar{1}$0). He claimed to have observed 15 distinct Raman lines with frequency shifts 452, 458, 614, 620, 638, 650, 989, 1038, 1082, 1088, 1109, 1136, 1142, 1158 and 1170 cm.$^{-1}$, some of which did not appear for certain orientations of the crystal. According to him, none of the three settings of the crystal tried by him gave the complete spectrum. This result has neither been confirmed nor contradicted by Roop Kishore (1942). From an analysis of the polarisation data Balakrishnan concluded that the lines with frequency shifts 452, 458, 650, 989 and 1170 cm.$^{-1}$ belonged to the symmetric class,

It is clear that the results obtained by the earlier investigators on the Raman effect in barytes are neither complete nor in agreement. It is therefore thought desirable to study the problem afresh using the very powerful ultra-violet technique which has yielded much useful information in the case of diamond, calcite, quartz, etc. (Krishnan, 1945). The use of the 2536·5 λ resonance radiation as exciter would enable one not only to record the first order spectrum of barytes in all its detail but also to investigate the nature of its second order spectrum about which nothing is known at present. The present investigation was undertaken with this object in view and also to confirm or disprove Balakrishnan's findings regarding the effect of crystal orientation on the frequency shifts of the Raman lines.

2. Details of the Experiment

From Sir C. V. Raman's personal collection of minerals two transparent specimens of barytes were chosen for the present study. The bigger crystal was in the form of a parallelepiped (10 × 8 × 5 cm.), with its faces parallel to the natural cleavage planes (001), (110) and (1$\bar{1}$0). It was used as such. The smaller specimen which had a natural *c* (001) face was cut and polished with its faces perpendicular to the axes of the optical ellipsoid. This crystal measured nearly 1 × 1 × 2·5 cm.

The optical arrangement employed for recording the Raman spectrum using the mercury resonance radiation as exciter has been described in Part I of this series (Krishnan, 1945). Using the E 3 quartz spectrograph a preliminary investigation was carried out in order to find any variations in the frequency shifts of the Raman lines for different settings of the crystal. Using the cut crystal three different spectrograms of the Raman effect were taken with the crystal illuminated successively along the *a*, *b* and *c* axes, the transversely scattered light being taken along *b*, *c* and *a* axes respectively. A comparative study of the three spectra recorded in juxta-position on the same negative showed that the frequency shifts of the Raman lines remain invariant, whereas the relative intensities of the lines depend on the orientation of the crystal. The experiment was repeated with the bigger crystal which had the natural cleavage faces and the same result was obtained. Balakrishnan's claim that none of the orientations of the crystal of barytes gave a complete Raman spectrum is therefore not substantiated by the results obtained by the author.

In order to get accurate measurements of the frequency shifts of the principal Raman lines, a Hilger E 1 quartz spectrograph which has a dispersion of about 50 wavenumbers/mm. in the 2536 λ region was used.

Using a slit width of 0·03 mm. and the bigger crystal, exposures of the order of 4 days were given to photograph the Raman spectrum showing the first order lines with reasonable intensity. The frequency shifts of the lines were evaluated by comparison with the superposed iron arc spectrum.

In order to record the second order spectrum the high speed low dispersion E 3 quartz spectrograph was employed. With a slit width of 0·03 mm. exposures of the order of two to three days were given to get an intense spectrogram. The frequency shifts of the more intense and easily identifiable second order lines were evaluated from measurements made on the spectrogram. Those of the feebler ones were estimated from the microphotometric record.

3. Results

A typical photograph of the Raman spectrum taken with the E 1 spectrograph together with its microphotometric record is reproduced in Fig. 1 in Plate I. The positions and the frequency shifts of the principal Raman lines are marked in Fig. 1 *b*. They are listed in Table I. The figures

Table I

Principal Raman lines of barytes

No.	Group	Frequency shifts in cm.$^{-1}$ author's value	Notations	Rasetti's value
1	Lattice	58·5 (6)	L_1	56·8
2	,,	64·0 (8)	L_2	62·2
3	,,	73·6 (10)	L_3	73·6
4	,,	88·3 (6)	L_4	88·3
5	,,	96·5 (4)	L_5	97·8
6	,,	127·4 (3)	L_6	127·3
7	,,	148·8 (3)	L_7	150·3
8	,,	151·4 (4)	L_8	
9	,,	189·7 (4)	L_9	189·8
10	Sulphate	452·9 (14)	ν_1	451·4
11	,,	462·2 (15)	ν_2	462·2
12	,,	617·1 (10)	ν_3	..
13	,,	630·3 (7)	ν_4	631·1
14	,,	648·3 (8)	ν_5	647·5
15	,,	988·6 (39)	ν_6	989·3
16	,,	1084·2 (6)	ν_7	1104·6
17	,,	1104·2 (5)		
18	,,	1139·1 (10)	ν_8	1141·4
19	,,	1144·8 (10)		
20	,,	1167·2 (8)	ν_9	1167·2

given in brackets represent visual estimates of the relative intensities of the lines. The direction of illuminaton was normal to the (001) face and the direction of observation was normal to the (110) face. Rasetti's values for the frequency shifts are shown in column 5. The author's results are in

close agreement with those of Rasetti except for the three doublets with frequency shifts 148·8–151·4 cm.$^{-1}$, 1084·2–1104·2 cm.$^{-1}$ and 1139·1–1144·8 cm.$^{-1}$ Rasetti treated them as single lines. The principal Raman line

TABLE II

Second order Raman lines of barytes

No.	Frequency shifts in cm.$^{-1}$	Assignment	Calculated frequency shifts
1	170	$L_3 + L_5$	170
2	246	$L_5 + L_7$; $L_5 + L_8$	245; 248
3	273	$L_6 + L_7$	276
4	293	$2L_7$	298
5	341	$L_8 + L_9$	341
6	518	$\nu_1 + L_2$	517
7	542	$\nu_1 + L_4$	541
8	750–800	$\nu_3 + L_6$; $\nu_4 + L_6$	744; 757; 766;
		$\nu_3 + L_7$; $\nu_5 + L_6$	775; 797; 799
		$\nu_5 + L_7$; $\nu_5 + L_8$	
9	900	$2\nu_1$	906
10	923	$2\nu_2$	924
11	967		
12	1216	$\nu_3 + L_3$	1215
13	1238	$2\nu_3$	1235
14	1267	$\nu_3 + \nu_5$	1266
15	1439	$\nu_6 + \nu_1$	1442
16	1450	$\nu_6 + \nu_2$	1451
17	1603	$\nu_6 + \nu_3$	1606
18	1970	$2\nu_6$	1978
19	2220	$\nu_7 + \nu_8$	2223

with the frequency shift of 617·1 cm.$^{-1}$ has been recorded for the first time. The 20 Raman frequencies tabulated above have been classified into two groups, namely, lattice spectrum denoted by L_1, L_2,.... L_9 and the spectrum of the SO_4 ions in the crystal denoted by ν_1, ν_2,.... ν_9.

An intense photograph of the Raman spectrum of barytes taken with the E 3 spectrograph is reproduced in Fig. 2 together with a spectrum of the mercury arc for purposes of comparison. The corresponding microphotometric records are shown in Fig. 3. The second order Raman lines can be clearly seen on the microphotometric record. Most of them can also be identified on the reproduced photograph. In addition to the 20 Raman lines belonging to the first order spectrum, there are not less than 18 Raman lines and one Raman band constituting the spectrum of the second order. The frequency shifts of these are listed in Table II. They have all been recorded as such for the first time. Roop Kishore (1942) reported the existence of only a band extending from 1198 cm.$^{-1}$ to 1300 cm.$^{-1}$ consisting of unresolved lines.

Of the second order lines, the Raman line with the frequency shift 967 cm.$^{-1}$ is the most intense one as it appears even in the lightly exposed photograph taken with the E 1 spectrograph. See Fig. 1. The pair of lines with frequency shifts 1216 cm.$^{-1}$ and 1238 comes next in the order of intensity.

As in the case of other crystals like calcite, gypsum, etc., the intensity of the 2536·5 λ line relative to that of its companion at 2534·8 λ is greater in the spectrum of the scattered light than in that of the direct arc. The enhanced intensity of the unmodified line can be attributed to the presence of Brillouin components which are not absorbed by the column of mercury vapour, compare the microphotometric records reproduced in Fig. 3.

4. Discussion

Barytes is an ionic crystal belonging to the orthorhombic bipyramidal class. The unit cell contains four molecules of $BaSO_4$, the space group is V_h^{13}. James and Wood (1925) carried out a detailed X-ray analysis of the crystal structure of barytes. Their results go to show that the SO_4 ions preserve their tetrahedral symmetry in the crystal.

Spectrum of the SO_4 ion.—The SO_4 ion in the free state has only four distinct modes of oscillation with frequency shifts 454 (2), 622 (3), 983 (1) and 1106 (3) cm.$^{-1}$ The figures given in brackets are the respective degeneracies. From group theoretical analysis Bhagavantam (1938) showed that in the case of anhydrite which belongs to the orthorhombic class the four distinct modes of oscillation characteristic of the free SO_4 ions split up into nine components in the crystal. We may expect to get similar results with barytes also which has a structure similar to that of anhydrite. With the disappearance of the degeneracy, the spectrum of barytes should exhibit all the nine lines characteristic of the SO_4 ion. Actually 11 frequency shifts are recorded in the first order spectrum all of which are attributable to the oscillations of the SO_4 ion. By comparing the values of the frequency shifts of barytes with those of the free SO_4 ion it is possible to identify seven out of the expected nine modes. These are denoted by ν_1, ν_2, ν_3.... ν_8 and ν_9 (see Table I). The remaining two fundamentals, namely ν_7 and ν_8 appear to have suffered a Fermi splitting due to accidental degeneracy giving rise to 4 Raman lines as indicated below. It is probably correct to take ν_7 as 1094 cm.$^{-1}$ which splits up into 1084 and 1104 cm.$^{-1}$ on account of the fact that the combination ν_2 (462·2) + ν_4 (630·3) falls on the top of ν_7. In same way, ν_8 which has a frequency shift of 1142 cm.$^{-1}$ splits up into two lines with frequency shifts 1139 and 1145 cm.$^{-1}$ since the combination of ν_8 (988·6) and L_8 (151·4), one of the lattice lines falls in the region of this doublet.

TABLE III

Raman frequencies of the SO_4 ion

In the free state	454 Double		622 Triple			983 Single	1106 Triple		
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
In barytes ..	452·9	462·2	617·1	630·3	648·3	988·6	1094	1142	1167
In anhydrite	415	499	609	628	674	1018	1108	1128	1160
In gypsum ..	415	492	618	622	672	1006	1115	1136	1144

The values of the frequency shifts of the nine Raman lines due to the internal oscillations of the SO_4 ions in barytes, anhydrite and gypsum are listed in Table III. The corresponding Raman frequencies of the free SO_4 ion are also included for comparison. The values of the frequency shifts for anhydrite were those reported by other workers. The values for gypsum were taken from Part II of this series (Krishnan, 1945). A comparative study of the frequency shifts of the SO_4 ion in barytes and anhydrite shows that the influence of the cation on the splitting of the degenerate frequencies 454 cm.$^{-1}$ and 622 cm.$^{-1}$ and on the enhancement of the totally symmetric oscillation frequency 983 cm.$^{-1}$ of the free SO_4 ion is inversely proportional to its atomic weight. Polarisation studies made by Rousset and Lochet (1945) show that in the case of gypsum the frequencies ν_1, ν_2, ν_4, ν_6 and ν_8 come under the symmetric class, whereas in the case of barytes Balakrishnan's measurements indicate that ν_1, ν_2, ν_5, ν_6 and ν_9 come under the symmetric class. The fact that out of the nine SO_4 lines of barytes, five come under symmetric class and four antisymmetric shows that the vibrating SO_4 ion possesses only as elements of symmetry a binary axis parallel to the binary axis of the crystal, although the ion has the full tetrahedral symmetry when the atoms are at rest.

The lattice spectrum.—Bhagavantam (1938) has shown that in anhydrite which has a structure similar to that of barytes there should be eighteen Raman active lattice oscillations. The recorded spectrum of barytes, on the other hand, consists of 9 lattice lines, *i.e.*, exactly half the theoretical number. Comparing the lattice spectrum of gypsum with that of barytes one finds that there is no striking similarity between the two except for the fact that both the spectra consist of sharp, intense and closely spaced lattice lines.

Combinations of the principal frequencies.—In the second order spectrum the overtones and combinations of all the fundamental frequencies listed

in Table I can appear. On this basis satisfactory assignments have been given to all the lines except one with frequency shift 967 cm.$^{-1}$ appearing in the second order Raman spectrum (see Table II). The calculated frequency shifts agree reasonably well with the observed values. Of the sulphate frequencies, the octaves of ν_1 (452·9), ν_2 (462·2), ν_3 (617·1) and ν_6 (988·6) are recorded as clearly resolved lines. There is indication of some unresolved lines in the neighbourhood of 1238 and 1267 cm.$^{-1}$ (see Fig. 3). These can be assigned as the octaves of ν_4 (630·3) and ν_5 (648·3). It is interesting to note that the octave of the most intense principal Raman line, namely, ν_6 (988·6 cm.$^{-1}$) is very weak compared to the octave of some of the other sulphate lines, *e.g.*, ν_1 (452·9 cm.$^{-1}$) or ν_2 (462·2 cm.$^{-1}$).

5. Infra-Red Spectrum

Comparatively little work has so far been done on the infra-red absorption spectrum of barytes. Schæfer and Schubert (1916) reported the existence of two reflection maxima in barytes, one at 8·30 μ (1204 cm.$^{-1}$) and the other at 8·93 μ (1120 cm.$^{-1}$). Matossi and Kindler (1934) investigated the infra-red absorption spectrum of barytes in the range from 2 μ to 16 μ. They observed two strong absorption bands at 9 μ and at 15·65 μ corresponding frequencies being 1100 cm.$^{-1}$ and 640 cm.$^{-1}$ These absorption bands might correspond to the observed Raman lines 630·3 and 1094 cm.$^{-1}$ which come under the antisymmetric class and hence active in the infra-red. The above authors have also reported the existence of two weak absorption bands at 12·35 μ (810 cm.$^{-1}$) and 10·81 μ (925 cm.$^{-1}$) in the infra-red. There are no first order Raman lines corresponding to these. The second order spectrum, on the other hand, exhibits two Raman lines with corresponding frequency shifts.

The author is grateful to Sir C. V. Raman for the loan of the crystals of barytes and also for his interest in the work. The author is also indebted to the authorities of the Annamalai University for the loan of the Hilger E 3 quartz spectrograph.

Summary

The previous work on the Raman effect in barytes has been briefly reviewed.

The Raman effect in natural crystals of barytes has been studied in detail using the 2536·5 λ mercury resonance radiation as exciter. The recorded spectrum consists of not less than 39 Raman lines nearly half of which have been recorded for the first time. Of these 20 lines belong to the first order Raman spectrum and are distributed as follows:—9 lattice lines and 11 lines

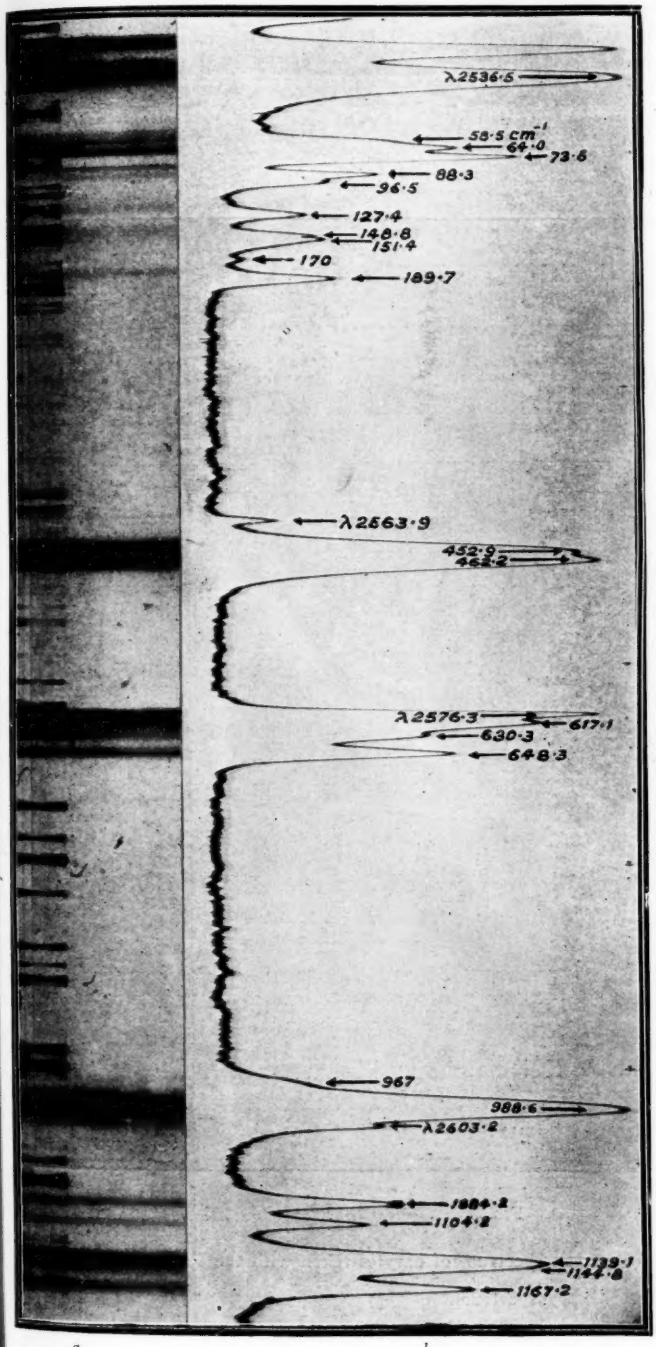

FIG. 1

(*a*) Raman spectrum of barytes taken with the E1 spectrograph; (*b*) its microphotometric record.

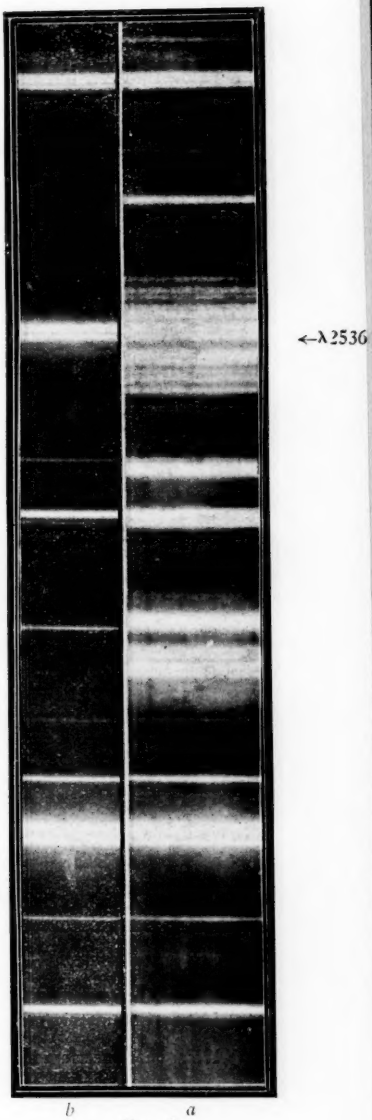

FIG. 2

(*a*) Raman spectrum of barytes taken with the E3 spectrograph. (*b*) Comparison spectrum of the mercury arc.

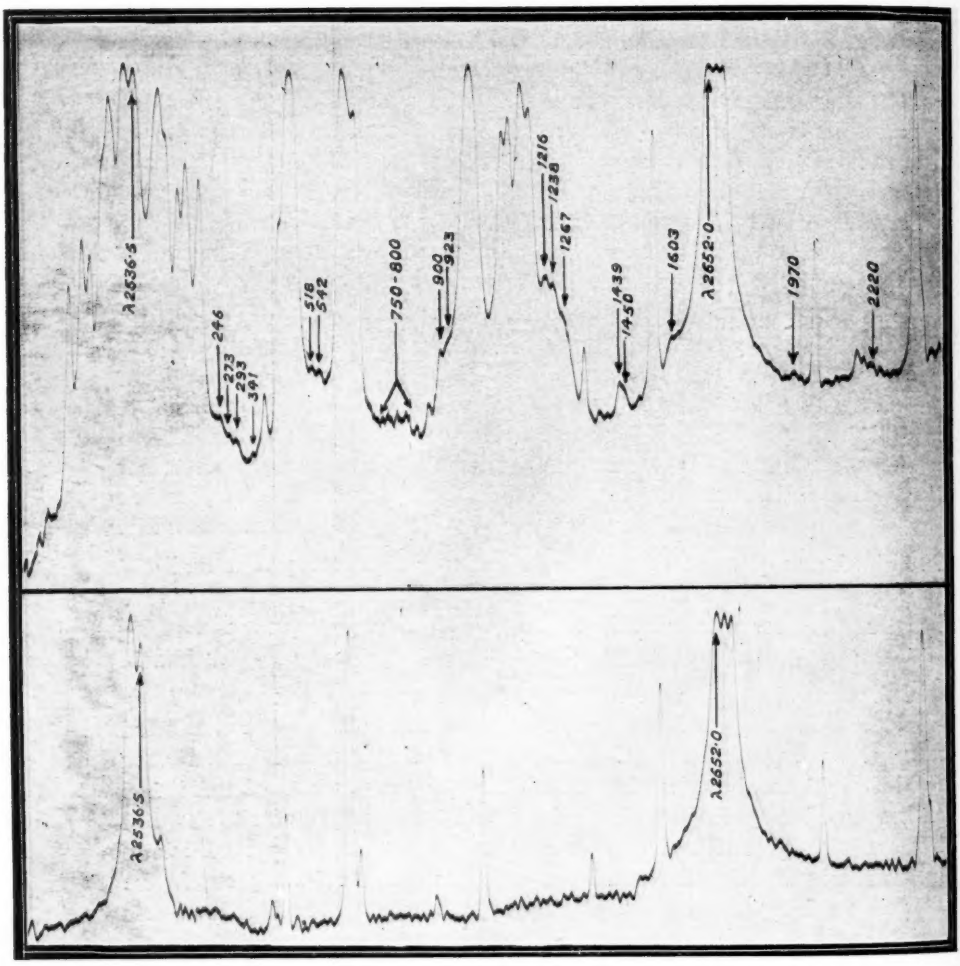

FIG. 3

(*a*) Microphotometric record of the Raman spectrum of barytes taken with the E3 spectrograph.

(*b*) Microphotometric record of the mercury spectrum.

due to the internal oscillations of the SO_4 ion. The frequency shifts of these lines have been accurately measured. The appearance of 11 Raman lines in the first order spectrum of the SO_4 ion has been satisfactorily explained on the basis of the lower order of symmetry of barytes crystal and also due to Fermi resonance splitting.

19 Raman lines of comparatively feeble intensity which constitute the second order spectrum have been assigned as octaves and combinations of some of the 20 principal Raman frequencies.

The frequencies corresponding to the maxima observed in the infra-red absorption spectrum of barytes have been compared with those observed in the Raman effect.

A complete bibliography on the Raman effect and infra-red studies in barytes is included.

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CONSTITUTION OF CANNABISCITRIN—PART II

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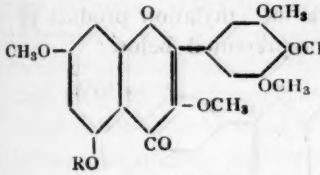
CANNABISCITRIN[1] is the main crystalline component of the flowers of *Hibiscus cannabinus*. It is a monoglucoside of cannabiscetin, a flavonol having six hydroxyl groups. When decomposed with aqueous alkali its hexamethyl ether yielded *O*-trimethyl-gallic acid. Thus four of the six hydroxyl groups of the flavonol could be definitely allotted to the positions 3, 3′, 4′ and 5′. The orientation of the other two as 5 : 8 was tentatively suggested, based on colour reactions. The aglucone was considered to be isomeric with myricetin and not identical with it mainly for the following reasons: (1) it gave the gossypetone reaction though not so readily as gossypetin and this was considered to be characteristic of compounds having hydroxyl groups in the *para*-positions 5 and 8; it further gave a display of colours in alkaline buffer solutions; (2) the methyl ether of cannabiscetin as originally obtained was noticed to have a higher melting point than that of myricetin though the melting points of cannabiscetin and its acetate agreed with those of myricetin and its acetate.

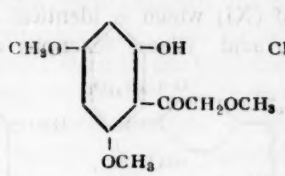
In a subsequent paper[2] the position of the sugar group was fixed as 3′. This was done by methylation of the glucoside, hydrolysis and fission of the product whereby 3-hydroxy-4 : 5-dimethoxy-benzoic acid was obtained and identified.

Further work has now been done with a view to obtain more definite information about the nature of the flavonol and its glucoside using improved methods of methylation and fission leading particularly to the isolation and identification of the ketonic decomposition product. The different methods of methylation that have been so far employed by different workers have been applied to the present case. The use of dimethyl sulphate and anhydrous potassium carbonate in anhydrous acetone solution has been found to be the most satisfactory and has given the best yields of the pure ether. The hexamethyl ether of cannabiscetin obtained in this way is found to melt at 156° agreeing with the melting point of myricetin methyl ether.[3] The higher melting product originally described could not be obtained again even by adopting the other methods and the older sample was not available for comparison due to loss during the transfer of our laboratories as a war measure. Whether this is antoher case of dimorphism found in certain other flavonol ethers could not therefore be settled.

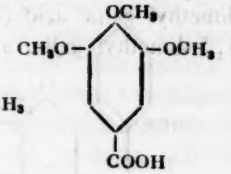
Since it has been our experience that the use of absolute alcoholic potash for the fission of methyl ethers gives much better results than older methods and is particularly suited for dealing with small quantities, this method has now been adopted for the fission of the hexamethyl ether of cannabiscetin (I). Besides trimethyl gallic acid (III) good yields of a ketonic product has been obtained and it has been identified as methoxy fisetol-dimethyl ether (II)[4] by a detailed study of its reactions and conversion into derivatives and also by comparison with a synthetic sample. This definitely established the position of the two hydroxyl groups in the benzopyrone part as 5:7 and not 5:8 and thus cannabiscetin should be the same as myricetin (VIII). The identity was established by the synthesis of myricetin and its derivatives according to the method of Kalff and Robinson[5] and comparison with cannabiscetin, its acetate and methyl ether. It should be noted here that the colour reactions with buffer solutions and *p*-benzoquinone which were originally considered to be characteristic of the 5 : 8 arrangement of hydroxyl groups are also given by flavonols containing three hydroxyls in the 3′: 4′: 5′ positions.



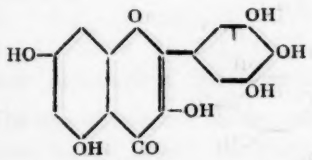
(I) R = CH_3
(IV) R = H



(II)



(III)



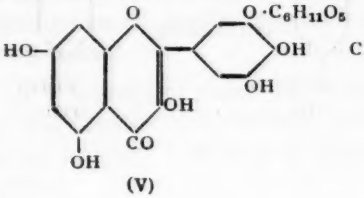
(VIII)

In the course of the experiments on the identification of cannabiscetin, methoxy-fisetol-dimethyl ether (ω : 4 : 6-trimethoxy-2-hydroxy acetophenone) was fused with the anhydride and sodium salt of trimethyl-gallic acid. There was partial demethylation during the condensation and the product was found to be 5-hydroxy-3 : 7 : 3′ : 4′ : 5′-pentamethoxyflavone (IV) or pentamethylmyricetin[3] obtained by Perkin by the partial methylation of myricetin.

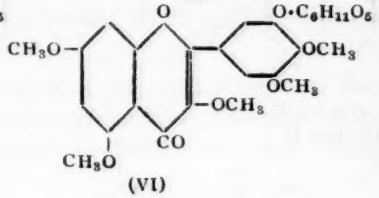
In the light of the identity of cannabiscetin with myricetin, the constitution of the glucoside, cannabiscitrin has been further investigated using the simpler

method of methylation. Though the glucoside is sparingly soluble in dry acetone, it could be successfully and fully methylated in this medium in a finely powdered condition by boiling with excess of dimethyl sulphate and potassium carbonate. The methylated glucoside could be obtained in a pure condition and hydrolysed to give a pentamethyl ether of cannabiscetin (myricetin) in good yield. Fission of this substance with alcoholic potash has yielded as one product methoxy-fisetol-dimethyl ether (II) showing conclusively that the sugar group is not present in the benzopyrone part. The acid decomposition product was identified to be 4: 5-dimethyl gallic acid (IX) by comparison with a sample synthesised according to the method of Shriner and McCutchen[6] thus establishing the constitution of the pentamethyl ether as (VII) and the constitution of the glucoside as (V) with the sugar unit in the side phenyl nucleus in position 3'.

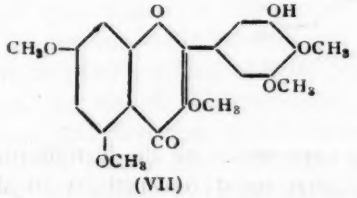
A more convenient method of establishing the exact constitution of the glucoside is to ethylate the above penta-methyl ether to give ethyl-pentamethyl-cannabiscetin (myricetin) (X) and subject this to fission. The reaction goes more smoothly yielding the same ketone (II) and 3-ethyl-4: 5-dimethyl gallic acid (XI) which is identical with the ethylation product of 4: 5-dimethyl gallic acid. These reactions are represented below:



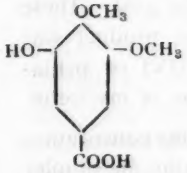
(V)



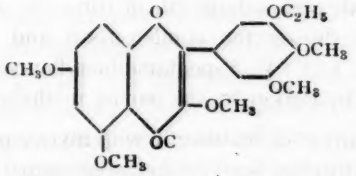
(VI)



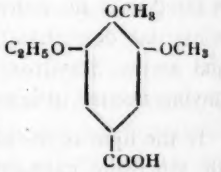
(VII)



(IX)



(X)



(XI)

Cannabiscitrin is, therefore, a new mono-glucoside of myricetin, the glucose group being in the 3′-position. Myricitrin[8] isolated by Perkin from *Myrica nagi* is a rhamnoside and the rhamnose unit is considered to be linked to the 3-position of the flavonol.

It is interesting to compare the flavonols present in the flower petals of the two closely related species of *Hibiscus*, *H. cannabinus* and *H. sabdariffa*. Botanically the plants resemble closely and they are also used for the same purposes, as acid vegetables and as sources of fibre. The *cannabinus* flowers contain myricetin as the flavonol, whereas hibiscetin is the main component of *sabdariffa* petals. Since the latter is 8-hydroxymyricetin, it appears that the species difference rests in the oxidation of the 8-position of the flavonol molecule.

Experimental

Hexamethyl cannabiscetin (I).—Cannabiscetin (1·0 g.), dissolved in dry acetone (100 c.c.), was treated with dimethyl sulphate (2·5 c.c.) and anhydrous potassium carbonate (20 g.) and the mixture boiled under reflux for 30 hours. After the completion of the reaction, the potassium salts were filtered off and washed with more acetone. The filtrate was concentrated and the residue treated with water (100 c.c.); the methyl ether then separated out completely during the course of one hour. It was twice crystallised from dilute alcohol when it came out in the form of colourless rectangular plates and prisms melting at 155-56°. It was insoluble in dilute sodium hydroxide solution and did not give any colour with alcoholic ferric chloride. The methyl ether exhibited a weak blue fluorescence in alcoholic solution. Yield: 1·0 g. (Found: C, 62·9; H, 5·7; OCH_3, 46·1; $C_{21}H_{22}O_8$ requires C, 62·7; H, 5·5; OCH_3, 46·3%.) The mixed melting point with myricetin hexamethyl ether was undepressed.

The use of benzene as the solvent in the above experiment also yielded the same methyl ether; the only difficulty was that cannabiscetin was not easily soluble in this solvent. Still the yield and the quality of the product were unaffected.

Other methods using (i) methyl iodide and anhydrous potassium carbonate in acetone solution, (2) methyl iodide and alcoholic potash and (3) dimethyl sulphate and alkali on cannabiscetin acetate, were examined in order to see if any higher melting ether could be obtained. But all of them yielded the same substance melting at 155–56°.

Decomposition of hexamethyl cannabiscetin with alcoholic potash : *Isolation of trimethyl gallic acid* (III) *and the ketone* (II).—Hexamethyl canna-

biscetin (1·0 g.) was boiled under reflux with absolute alcoholic potash (30 c.c. of 8%) for six hours under anhydrous conditions. At the end of the period as much of the alcohol as possible was distilled off and the residue dissolved in water. The aqueous solution was then filtered from a little insoluble impurity and the clear filtrate acidified with dilute sulphuric acid with cooling. The precipitated solid was then thrice extracted with ether and the combined ether solution shaken with 5% sodium bicarbonate to remove the acid part (A). On evaporating the ether solution the required ketone was obtained. It was crystallised twice from dilute alcohol when it came out in the form of thin colourless plates melting at 104–05°. The yield of the pure ketone was 0·34 to 0·38 g. It could also be crystallised from hot water. It dissolved easily in aqueous sodium hydroxide forming a pale yellow solution and gave a greenish brown colour with alcoholic ferric chloride. The mixed melting point with an authentic sample of 2-hydroxy-ω-4: 6-trimethoxy-acetophenone was undepressed. (Found: C, 58·6; H, 6·5; OCH_3, 40·9; $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2; and OCH_3, 41·2%.)

The *dinitrophenylhydrazone* was obtained by heating a mixture of the above ketone (0·1 g.) and 2: 4-dinitrophenylhydrazine (0·2 g.) dissolved in alcohol (10 c.c.), on a water-bath for half an hour. The phenylhydrazone separated out on cooling; it was washed with dilute hydrochloric acid and crystallised from alcohol when it came out in the form of orange-red micro-crystals melting at 160–62°. It was soluble in aqueous alkali to give an orange-red solution. (Found: C, 49·9; H, 4·7; $C_{17}H_{18}O_8N_4$ requires C, 50·2; H, 4·4%.)

The clear bicarbonate solution (A) obtained above was neutralised with dilute hydrochloric acid. The precipitated solid was repeatedly crystallised from hot water using a little animal charcoal. It came out in the form of colourless rectangular plates, melting at 167–68° and was identified as trimethyl gallic acid. The mixed melting point with an authentic sample of trimethyl gallic acid was undepressed. (Found: C, 56·7; H, 5·7; OCH_3, 44·1; $C_{10}H_{12}O_5$ requires C, 56·6; H, 5·7 and OCH_3, 43·9%.)

ω: 2: 4: 6- *Tetramethoxy-acetophenone.*— 2-Hydroxy-ω-4: 6-trimethoxy-acetophenone (0·2 g.) was methylated in acetone solution with dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (5·0 g.). The product was crystallised from dilute alcohol when it came out in the form of colourless rectangular plates melting at 151–52°. It was insoluble in dilute sodium hydroxide solution and did not give any colour with alcoholic ferric chloride. (Found: C, 60·1; H, 6·9; OCH_3, 51·9; $C_{12}H_{16}O_5$ requires C, 60·0; H, 6·7 and OCH_3, 51·7%.)

Comparison of cannabiscetin and myricetin (synthetic).—The following properties were compared and found to be identical. The flavonols decomposed above 350° and gave a dark brown colour with alcoholic ferric chloride; the hexamethyl ethers melted at 155–56° and the hexa-acetates at 220–21°. The colour reactions in alkaline buffer solutions were also identical. With freshly made buffer solutions, the appearance of pure blue has now been noticed even with a slightly lower pH. This may be due to changes in the buffer solutions during storage.

Condensation of hydroxy-fisetol trimethyl ether (II) *with the anhydride and the sodium salt of trimethyl gallic acid: Preparation of 5-Hydroxy-3:7:3′:4′:5′-pentamethoxy-flavone (IV).*—2-Hydroxy-ω:4:6-trimethoxy acetophenone (1·0 g.) was intimately mixed with the dry anhydride (6 g.) and the sodium salt of trimethyl gallic acid. The product was heated at 180° for 6 hours *in vacuo*. The hard mass was then broken up and dissolved in alcohol (150 c.c.) and while boiling, an aqueous potassium hydroxide solution (8 g. in 15 c.c.) was added during the course of 20 minutes to decompose the excess of the anhydride. The alcohol was then completely removed under reduced pressure and the residue dissolved in water. A small quantity of a solid (S) separated out. It was filtered and the filtrate was then saturated with carbon dioxide. The pale yellow product was repeatedly crystallised from alcohol when it came out as very pale yellow stout needles melting at 140–41°. This product corresponded to the pentamethyl ether of myricetin (m.p. 138–39°) recorded by Perkin.[3] In bulk, the substance appeared yellow. It gave an olive green colour changing to brown with alcoholic ferrric chloride and did not exhibit any visible fluorescence in alcoholic solution. (Found: C, 62·0; H, 5·3; OCH_3, 40·1; $C_{20}H_{20}O_8$ requires C, 61·9; H, 5·2 and OCH_3, 40·0%.) On working up solid (S) some more of the above 5-hydroxy compound was obtained.

Methylation of the above 5-hydroxy-flavone with excess of dimethyl sulphate and anhydrous potassium carbonate in acetone solution yielded the hexamethyl ether of myricetin which crystallised from dilute alcohol as colourless rectangular plates and prisms and melted at 155–56°.

Acetate of cannabiscitrin.—This was conveniently prepared by boiling the glucoside with acetic anhydride and a drop of pyridine, and crystallising the colourless product by dissolving in cold acetone and adding enough ethyl alcohol to start crystallisation. When prepared in this manner, it appeared as colourless needles and melted to a transparent liquid at 194°. (Found: C, 54·4; H, 4·4; $C_{39}H_{38}O_{22}$ requires C, 54·5; H, 4·4%.)

Methylation of cannabiscitrin: Preparation of the methylated glucoside (VI).—Finely powdered cannabiscitrin (4·0 g.) was suspended in dry acetone (200 c.c.), treated with dimethyl sulphate (6·0 g.) and anhydrous potassium carbonate (25 g.) and the mixture boiled under reflux for 30 hours. It was occasionally shaken to bring any unreacted cannabiscitrin into solution. The acetone solution was filtered, washed with more acetone and then concentrated when colourless crystals of the methylated glucoside separated out. It was recrystallised from methyl alcohol when it came out as shining needles and rectangular plates melting at 149–50°. It was insoluble in dilute alkali and did not give any colour with alcoholic ferric chloride. (Found: C, 56·4; H, 5·3; $C_{28}H_{30}O_{13}$ requires C, 56·7; H, 5·5%.)

Hydrolysis of the methylated glucoside: Isolation of pentamethyl cannabiscetin (*myricetin*) (VII).—The whole of the product obtained above (VI) was boiled under reflux with 7% sulphuric acid (200 c.c.) for 2 hours. The hot solution was filtered through a plug of cotton-wool to remove a small quantity of insoluble impurity that had separated out. The pentamethyl ether crystallised out almost completely on cooling. It was recrystallised twice from alcohol when it came out in clusters of colourless needles. The correct melting point of this compound is 220–22°. It did not give any colour with alcoholic ferric chloride, but dissolved easily in dilute sodium hydroxide forming a pale yellow solution with no fluorescence. Yield, 1·76 g. from 4 g. of cannabiscitrin. It developed a pale pink fluorescence in neutral alcoholic solution after some time. (Found: C, 61·5; H, 4·8; OCH_3, 40·2; $C_{20}H_{20}O_8$ requires C, 61·9; H, 5·2 and OCH_3, 40·0%.)

The above pentamethyl cannabiscetin (0·5 g.) was dissolved in acetone (20 c.c.) and methylated by boiling for 10 hours with excess of dimethyl sulphate and anhydrous potassium carbonate. The product was crystallised from dilute alcohol when it came out as colourless rectangular plates melting at 154–56° and was found to be identical with the hexamethyl cannabiscetin obtained by direct methylation.

Decomposition of the above pentamethyl ether (VII) *with alcoholic potash: Isolation of* 4: 5-*dimethyl gallic acid* (IX) *and the ketone* (II).—Pentamethyl cannabiscetin (1·0 g.) was boiled under reflux with absolute alcoholic potash (30 c.c. of 8%) for a period of six hours. The product was worked up as before into the sodium bicarbonate soluble part (acid part) and the ketonic part. On crystallisation from alcohol, the ketone came out as colourless rectangular plates, melting at 104–05°. Mixed melting point with 2-hydroxy-ω ; 4: 6-trimethoxy acetophenone was undepressed.

The bicarbonate solution was acidified and repeatedly extracted with ether; the residue obtained on evaporating the ether solution was twice crystallised from hot water using a little animal charcoal when it came out as rectangular plates and prisms melting at 192–94°. It was found to be identical with 4: 5-dimethyl gallic acid, the mixed melting point with an authentic sample of 4: 5-dimethyl gallic acid being undepressed. (Found: C, 54·7; H, 5·4; OCH_3, 31·2; $C_9H_{10}O_5$ requires C, 54·5; H, 5·1 and OCH_3, 31·3%.)

*3′-Ethyl-*3 : 5 : 7 : 4′ : 5′*-pentamethyl cannabiscetin (myricetin)* (X).—The above pentamethyl cannabiscetin was ethylated with ethyl iodide and anhydrous potassium carbonate in acetone solution. The product was worked up as before and the ethyl ether was twice crystallised from dilute alcohol when it came out as stout rods and rectangular plates, melting at 155–56°. A mixed melting point with hexamethyl myricetin was considerably depressed. The product was insoluble in aqueous alkali and did not give any colour with alcoholic ferric chloride.

Decomposition of ethyl-pentamethyl cannabiscetin (X) *with alcoholic potash: Isolation of the ketone* (II) *and 3-ethyl-*4 : 5*-dimethyl gallic acid* (XI).—The ethyl pentamethyl ether (1·0 g.) was subjected to fission with alcoholic potash following the procedure already described. The ketonic part was found to be identical with 2-hydroxy-ω : 4 : 6-trimethoxy-acetophenone. The acid was crystallised from hot water using a little animal charcoal when it came out as colourless rectangular plates and prisms melting at 164°. It was identified as 3-ethoxy-4 : 5-dimethoxy-benzoic acid. The mixed melting point with an authentic sample of 3-ethoxy-4 : 5-dimethoxy-benzoic acid, prepared as given below was undepressed. (Found: C, 58·6; H, 6·4; $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2%.)

4 : 5-Dimethyl gallic acid[6] (1·0 g.) was ethylated using ethyl iodide (2 c.c.), anhydrous potassium carbonate and anhydrous acetone. The ether ester was obtained as a viscous liquid and it was hydrolysed by boiling with sodium hydroxide solution (20 c.c. of 20%) for one hour. The clear solution was then acidified and the solid product crystallised from hot water when it came out as colourless rectangular plates and prisms melting at 164°. (Found: C, 58·5; H, 6·4; $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2%.)

Summary

The methylation of the glucoside, cannabiscitrin and of the aglucone, cannabiscetin has now been effected by a more efficient method and the fission products examined. As the result cannabiscetin has been identified

as myricetin and the identity has been confirmed by comparison of the flavonol and its derivatives with synthetic samples. It is noted that the reactions of flavonols having the pyrogallol side-phenyl nucleus exhibit many similarities with those given by flavonols having the 5: 7: 8-arrangement of hydroxyl groups. The condensation of hydroxy-fisetol-trimethyl ether with the anhydride and sodium salt of gallic acid yields pentamethyl-myricetin instead of the expected hexamethyl ether, partial demethylation having taken place in the 5 position during the course of the condendation.

Methylation of the glucoside, cannabiscitrin yields a pentamethyl ether which forms on hydrolysis pentamethyl cannabiscetin (myricetin). Alkali fission of this compound gives the same ketone as the hexamethyl ether. The acid part is identified as 4: 5-dimethyl gallic acid, thus locating the position of the sugar group definitely in the 3′ position of the flavonol. This result has been confirmed by ethylating the pentamethyl cannabiscetin and subjecting the ethyl ether to fission with alkali. Besides the ketone already mentioned, the acid decomposition product is found to be 3-ethyl-4: 5-dimethyl gallic acid by comparison with a synthetic sample. The synthesis of the ethyl-dimethyl gallic acid is described.

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3. Perkin .. *J. C. S.*, 1902, **11**, 204.
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STUDIES IN THE FRIEDEL-CRAFTS REACTION

Part VIII. The Action of Acetic Anhydride on Methyl-γ-Resorcylate

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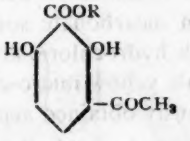
Received December 14, 1945

In continuation of the previous work of Desai and Radha,[1] the action of acetic anhydride on methyl-γ-resorcylate in presence of anhydrous aluminium chloride has been studied. This condensation afforded methyl-2 : 6-dihydroxy-3-acetyl-benzoate (I, R = CH_3) and 2: 6-dihydroxy-3-acetyl-benzoic acid (I, R = H). The ester and the acid both were characterized by the formation of 2: 4-dinitrophenyl-hydrazones and semicarbazones. The ester (I, R = CH_3) on hydrolysis afforded the corresponding acid (I, R = H), which on decarboxylation gave resacetophenone, thus establishing the structures of both the acid and the ester. From the yield of the ester and the acid and the rate at which the reaction proceeded it was noted as expected that methyl-γ-resorcylate was more reactive than its isomer methyl-β-resorcylate.



(I)

Experimental

Methyl-2: 6-dihydroxy-3-acetyl-benzoate (I, R = CH_3) and 2: 6-dihydroxy-3-acetyl-benzoic acid (I, R = H). Finely powdered anhydrous aluminium chloride (3 g.) was dissolved in dry methyl-γ-resorcylate (2 g.) in nitrobenzene with constant shaking. Acetic anhydride (2·5 c.c.) was then added to the mixture slowly and the mixture kept at room temperature for 24 hours, with an air condenser and a calcium chloride guard-tube attached to the flask. It was then heated for 3 hours on a water-bath and the mixture cooled. The aluminium chloride was decomposed by adding pieces of ice and hydrochloric acid to the reaction mixture and the nitrobenzene steam distilled. The sticky paste obtained on cooling was worked up in the usual manner with sodium bicarbonate solution (5 per cent.) when part of it went into solution with effervescence, and a fraction remained insoluble. The

latter was washed with water and crystallized from very dilute hot alcohol in long golden-yellow needles, m.p. 137-38° C. (Found: C, 56·9, H, 4·4; $C_{10}H_{10}O_5$ requires C, 57·1; H, 4·8 per cent.) It gave an intense red colouration with alcoholic ferric chloride and was very soluble in all the common solvents like alcohol, acetone and methyl alcohol.

The sodium bicarbonate soluble portion was acidified with hydrochloric acid, and extracted with ether, when pale yellow micro-crystals were obtained on the evaporation of the solvents, m.p. 210-12.° (Found: C, 54·8; H, 4·0; $C_9H_8O_5$ requires C, 55·1; H, 4·1 per cent.) It gave effervescence with sodium bicarbonate solution and a wine-red colouration with alcoholic ferric chloride.

The 2: 4-*dinitrophenyl-hydrazone* prepared in the usual manner crystallized in orange-red micro-crystals from glacial acetic acid m.p. 293° (decomp.). (Found: N, 14·2; $C_{16}H_{14}O_8N_4$ requires N, 14·4 per cent.)

The Semicarbazone prepared as usual, crystallized in very pale-yellow, shiny micro-crystals from boiling alcohol, m.p. 273° (decomp.). (Found: N, 15·4; $C_{11}H_{13}O_5N_3$ requires N, 15·7 per cent.)

2: 6-*dihydroxy*-3-*acetyl-benzoic acid* (*I*, $R = H$).— Methyl 2: 6-dihydroxy-3-acetyl-benzoate (0·3 g.) was hydrolysed in alcoholic alkaline solution in the usual manner. The solid obtained on acidifying with hydrochloric acid, was purified through sodium bicarbonate solution (5%). The yellow solid obtained on acidification with hydrochloric acid was washed and crystallized from dilute hot alcohol in pale yellow micro-crystals, m.p. 209–10°. Mixed melting point with the previously obtained acid was unaltered.

Decarboxylation of 2: 6-*dihydroxy*-3-*acetyl-benzoic acid* (0·2 g.) by heating in a sealed tube with acidulated water (10 c.c.) at 160–70° for 5 to 6 hours yielded a sticky paste. This was triturated with sodium bicarbonate solution and the insoluble portion crystallized from alcohol in yellow needles, m.p. 145–46°. Mixed melting point with an authentic specimen of resacetophenone was undepressed.

Summary

The action of acetic anhydride on methyl-γ-resorcylate in presence of anhydrous aluminium chloride afforded methyl-2: 6-dihydroxy-3-acetyl-benzoate and 2: 6-dihydroxy-3-acetyl-benzoic acid.

Reference

1. Desai and Radha .. *Proc. Ind. Acad. Sci.*, 1940, 12 A, 46.

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